"STUDIES ON THE REACTIVITY OF DEPOSITED CARBON"

A thesis submitted to the University of Glasgow in accordance with the regulations governing the award of the degree of Doctor of philosophy.

by

MUHAMMED RAHMAT ULLAH

Department of Pure and Applied Chemistry,
Chemical Technology Section,
Fuel Science Laboratories,
University of Strathclyde,
Glasgow, C.1.

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SUMMARY

The purpose of this work was to study the reactivity to carbon dioxide of carbon deposited by the thermal cracking of methane on metallic iron powder, with a view to evolving a process for the production of synthesis gas from natural gas.

The various methods of carbon-reactivity measurement and type of carbon available for gasification processes are discussed. Existing processes which utilise natural gas fo the production of synthesis gas are criticised and the benefits of a process in which separate streams of hydrogen and of carbon monoxide are produced continuously from natural gas are indicated. Consideration is given to the state of knowledge on the thermodynamics and kinetics of the thermal decomposition of methane and of Boudouard reaction, and to the published evidence for the enhanced reactivity of deposited carbon as compared with β-graphite.

As a basis for comparison a number of preliminary experimental studies have been made of the reactivity to carbon dioxide of powdered metallurgical coke in both fixed and fluidized beds and the effects of reactor temperature, gas flowrate, and the disposition of the bed. The results obtained were found to agree well with published data.

A large scale laboratory fluidized bed gasifier has been developed together with a system of two katharometers to give continuously a complete analysis of a gas containing carbon dioxide, carbon monoxide and nitrogen. This reactor was supplied with powdered haematite iron ore which was reduced to metallic iron in the fluidized state with hydrogen. The iron powder was fluidized with a mixture of nitrogen and methane at about 1300°F, to deposit carbon on the iron. The iron-carbon mixture was then fluidized with a mixture of carbon dioxide and nitrogen to gasify the carbon. The exit gas analysis and the rate of gasification of the carbon and the rate of oxygen absorption by the iron were all studied under a variety of conditions of temperature and inlet carbon dioxide partial pressure.

It was found that for gasification temperatures in the range of 1000 to 1300°F, the concentration of carbon monoxide in the exit gas was much in excess of that predicted by the Boudouard equilibrium over graphite. The values obtained corresponded to excess free energies for deposited carbon of the order of 1300 to 3000 calor's per gram mole. The exit gas analysis was dependent on the partial pressure of the inlet carbon dioxide, the highest value of the equilibrium ratio being obtained with a low concentration.

The rate of gasification of the carbon was found to be a constant for large ranges of carbon-iron ratio on the bed.

It was also shown that the reactivity of the carbon to carbon dioxide was dependent on the temperature at which the iron substrate had been reduced with hydrogen.

When air was used in place of carbon dioxide the exit gas showed negligible oxygen content indicating that comple utilization of the oxygen had taken place.

The rate of uptake of oxygen by the bed was studied and calculations made of the proportion of the input carbon dioxide which gasified the carbon and the proportion which oxidised the iron. It was suggested that if the gasificati temperature was increased to 1400°F, the absorption of oxygen by the iron became a small fraction of the oxygen leaving the gasifier as carbon monoxide.

The high concentration of carbon monoxide produced at a relatively low temperature suggest that this process may well be worthy of industrial exploitation for synthesis gas production.

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CONTENTS

SUMMARY i

LIST OF SYMBOLS AND ABBREVIATIONS iv

1. INTRODUCTION

1.1. Carbon reactivity 1

1.2. Methods of measurements of reactivity 2

1.2.1. Fuel Research method 2

1.2.2. Müller and Jandl rapid method.. 3

1.2.3. Critical air blast (C.A.B.) method 4

1.2.4. Modified ignition method 4

1.3. Physical properties influencing carbon reactivity 4

1.4. Types of carbon available for gasification 6

1.5. Synthesis gas production and its value 7

1.6. The potential of natural gas 9

1.7. The manufacture of synthesis gas from natural gas 11

1.7.1. Catalytic steam-reforming 11

1.7.2. Partial oxidation process 12

1.7.3. Limitations of the above processes 12

1.7.4. Requirements of an ideal process and the reactions involved 13

1.8. Purpose of research 14
1.9. Theory of methane decomposition 16
1.9.1. Thermodynamics 16
1.9.2. Kinetics and catalysts 16
1.10. Theory of Boudouard reaction 19
1.10.1. Thermodynamics 19
1.10.2. Kinetics and catalysts 20
1.11. Quasi-equilibria and free energy 24
2. Preliminary fixed-bed studies.
2.1. Preparation of coke powder and iron catalyst 27
2.2. Fixed-bed gasification apparatus 29
2.2.1. Furnace 30
2.2.2. Reaction tube 30
2.2.3. Gas metering 30
2.2.4. Gas analysis apparatus 31
2.3. Experimental procedure 31
2.4. Evaluation of "equilibrium ratio" 32
2.5. Calculation of residence time 33
2.6. Experimental results 34
2.6.1. Horizontal reaction tube 34
2.6.2. Vertical reaction tube 37
2.6.3. Sample calculations 41
2.6.4. Reaction with carbon deposited on iron 43
2.6.5. Graphical presentation of experimental results 46
2.7. Discussion of results 47

3. Fluid-bed studies in a mild steel bench scale reactor.

3.1. The development of fluidization and its utility 53

3.2. The mechanism of fluidization 55

3.3. Bench scale apparatus 56

3.3.1. Reactor 56

3.3.2. Gas preheater 56

3.3.3. Furnace 57

3.3.4. Gas metering 57

3.3.5. Gas cleaning 57

3.3.6. Gas analysis 57

3.3.7. Temperature measurement 58

3.4. Pressure-drop-flow diagram for fluidized bed 58

3.5. Experimental procedure 58

3.6. Discussion of results 59

4. Fluid-bed gasification studies in stainless steel reactor.

4.1. Apparatus requirements 66

4.2. Gasification apparatus and ancillary equipments 67

4.2.1. Stainless steel reactor 68

4.2.2. Heat supply system 70

4.2.3. Gas supply system 71

4.2.4. Gas metering instruments 72

4.2.5. Exit-gas cleaning system 72
4.2.6. Exit-gas sampling system 73
4.2.7. Gas analysing system 73
4.2.8. Fluid-bed pressure measuring equipment 74
4.3. Expansion characteristics of fluid-bed 75
4.4. Temperature distribution in the reactor ... 76
4.5. Pressure-drop-flow diagrams for fluidized bed 76
4.6. Calculation of off-gas analysis 78
4.6.1. Arrangements of Katharometers 78
4.6.2. Principles of Katharometer measurement 78
4.6.3. Principles of gas composition calculation 79
4.7. Experimental results 84
4.7.1. Attempts to gasify coke carbon 84
4.7.2. Reduction of a fluidized bed of iron ore 84
4.7.3. Reaction of carbon dioxide with reduced iron in the fluidized bed.. 85
4.7.4. Preliminary attempts to deposit carbon on reduced iron and its removal with carbon dioxide 90
4.7.5. Systematic carbon deposition and subsequent gasification 93

4.7.6. Principles of carbon deposition calculation 94

4.7.7. Comparison of actual carbon deposition with theory 102

4.7.8. Principles of carbon removal calculation 104

4.7.9. Calculation of oxygen taken up by the bed 106

4.7.10. Gasification runs and results obtained 107

5. General discussion.

5.1. Boudouard equilibrium 133

5.2. Rate of carbon gasification 136

5.3. Rate of oxygen absorption by the bed 139

5.4. Composition of bed at the end of run 140

5.5. Efficiency of carbon dioxide utilization 141

5.6. Suggestions for further work 143

REFERENCES.

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A large scale laboratory fluidized bed gasifier has been developed together with a system of two katharometers to give continuously a complete analysis of a gas containing carbon dioxide, carbon monoxide and nitrogen. This reactor was supplied with powdered haematite iron ore which was reduced to metallic iron in the fluidized state with hydrogen. The iron powder was fluidized with a mixture of nitrogen and methane at about 1300°F, to deposit carbon on the iron. The iron-carbon mixture was then fluidized with a mixture of carbon dioxide and nitrogen to gasify the carbon. The exit gas analysis and the rate of gasification of the carbon and the rate of oxygen absorption by the iron were all studied under a variety of conditions of temperature and inlet carbon dioxide partial pressure.

It was found that for gasification temperatures in the range of 1000 to 1300°F, the concentration of carbon monoxide in the exit gas was much in excess of that predicted by the Boudouard equilibrium over graphite. The values obtained corresponded to excess free energies for deposited carbon of the order of 1300 to 3000 calories per gram mole. The exit gas analysis was dependent on the partial pressure of the inlet carbon dioxide, the highest value of the equilibrium ratio being obtained with a low concentration.

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When air was used in place of carbon dioxide the exit gas showed negligible oxygen content indicating that complete utilization of the oxygen had taken place.

The rate of uptake of oxygen by the bed was studied and calculations made of the proportion of the input carbon dioxide which gasified the carbon and the proportion which oxidised the iron. It was suggested that if the gasification temperature was increased to 1400°F, the absorption of oxygen by the iron became a small fraction of the oxygen leaving the gasifier as carbon monoxide.

The high concentration of carbon monoxide produced at a relatively low temperature suggest that this process may well be worthy of industrial exploitation for synthesis gas production.

LIST OF SYMBOLS AND ABBREVIATIONS

b	=	moles of methane decomposed.
c	=	moles of carbon dioxide reacted.
"C_1"	=	weight of carbon deposited in time interval, gms.
"C_2"	=	weight of carbon deposited up to the end of a cycle, gms.
ΔC	=	lb-atoms of carbon removed in time t minutes.
"CO_2"	=	per cent carbon dioxide in outlet gas.
"CO"	=	per cent carbon monoxide in outlet gas.
d_1 and d_2	=	recorder deflection.
D_1	=	diameter, ft. or inches.
D	=	total dilatation.
ΔF	=	free energy change, cal/gm.mole.
G	=	total weight of carbon deposited in t minutes time, lb.
G/t	=	rate of carbon deposition, lb/min.
I_1	=	percentage of iron content in the bed before run.
I_2	=	percentage of iron content in the bed after run.
K	=	Boudouard equilibrium constant.
K_1	=	Katharometer factor.
L	=	length, ft. or inches.
m	=	number of moles of impure methane fed to the reactor.
n	=	moles of nitrogen fed to the reactor.
ΔO	=	lb-atoms of oxygen absorbed in time t_1 minutes.
"O_1"	=	weight of oxygen absorbed by the bed in time interval, gms.

"O_2" = weight of oxygen absorbed by the bed up to the end of total time of a cycle, gms.

p_1 = average pressure for inlet gas during carbon deposition, inches of water gauge.

p_2 = average pressure for inlet gas during gasification, inches of water gauge.

p_{CO_2} = partial pressure of carbon dioxide.

p_{CO} = " " " " monoxide.

q = uncorrected equivalent per cent carbon dioxide (Katharometer recorder reading).

R = gas constant, cal deg^{-1} $mole^{-1}$.

t and t_1 = duration of a cycle, minutes.

T = room temperature °C.

T_1 = absolute temperature, °K.

V = flowrate, ft^3/min.

V_1 = inlet flowrate of methane, ft^3/min.

V_2 = inlet flowrate of nitrogen, ft^3/min.

V_3 = total inlet flow during deposition, ft^3.

V_4 = inlet flowrate of gasification mixture, ft^3/min.

V_5 = total outlet flow in a time interval, ft^3.

W = weight of materials, gms. or lb.

x = moles of carbon dioxide in inlet gas.

y = moles of carbon dioxide decomposed.

"Y" = per cent inlet carbon dioxide decomposed.

Z = corrected equivalent per cent carbon dioxide (Katharometer recorder reading).

α, β and γ = constants.

ρ = true density, gms/cm^3 or lb/ft^3.

1. INTRODUCTION

1.1. Carbon Reactivity

The gasification of coke at elevated temperature with steam to form blue water gas is frequently the first step in the production of so-called "synthesis gas". While the composition of this gas depends on the nature of the gasifying fluid, e.g. steam alone, or steam and oxygen, and on the temperature and pressure in the gasifier, the rate at which it is produced at a given required composition depends on the "reactivity" of the coke.

The reactivity of coke or carbon is simply the extent to which it reacts with the gas under consideration, in a given time and at a given temperature.

A considerable amount of study has been devoted to carbon reactivity. While it is obvious that any reacting gas may be employed for measurements, most workers reserve the term "reactivity", as applied to carbon, for studies of its reaction with carbon dioxide[1-13].

Chou and Orming[14] report that a higher precision of reactivity measurement is possible when using carbon dioxide. This is due to the better adiabatic control possible with an endothermic reaction. Thring and his co-workers[15] prefer carbon dioxide for fuel reactivity

measurement to methods based on ignition limits, because carbon dioxide conversion at 950°C is a direct measure of rate of reaction. At this temperature the reaction is chemically controlled and therefore it gives a direct measure of the apparent "activation energy" of the carbon.

The reactivity of carbon has been defined by the Fuel Research Board[13] as "the number of millilitres of carbon monoxide formed from 100 ml of carbon dioxide" under certain definitely specified conditions.

1.2. Methods of measurement of reactivity.

There are several methods for the measurement of the reactivity of carbon, of which the following are widely used.

1.2.1. Fuel Research method.[13] This method measures the reactivity of carbon in terms of the extent of completion of the reaction

$$C + CO_2 = 2\ CO$$

when the equilibrium concentration of carbon monoxide is 97.4%. A standard volume of graded carbon (7 ml of 10 - 20 I.M.M. test sieve size) is maintained at 950°C and a current of pure carbon dioxide is passed through at the rate of 5 ml per minute. The carbon monoxide formed is then measured.

Three values are recognised from this experiment as given below:

R.I. is the number of millilitres of carbon monoxide formed per 100 ml of carbon dioxide. It is therefore the initial

reactivity and has a limit at the Boudouard equilibrium concentration of 197.4 ml.

R.II. is an apparently constant value which is reached after the expulsion of the volatile matter.

R.III. is a lower constant value reached after the continued action of the carbon dioxide on the sample of carbon.

1.2.2. Müller and Jandl rapid method.[16] In this method, a constant stream of pure carbon dioxide, at the rate of 2 litres per hour, is fed to the reactor, a quartz tube, heated by a furnace. The flow of carbon dioxide is metered through a flowmeter. A quartz boat inside the reactor tube holds the sample of carbon. The temperature of the reaction is kept at 900 $\pm$ 5°C. The product gases are cooled in a water-cooled coil and metered through another flowmeter before going to the exhaust. The flowmeters make it possible to have a continuous reading of the gas composition. The reactivity of the carbon is given by the formula

$$R = 100 \frac{Q_1}{Q_2}$$

where, R = percent reactivity

Q_1 = volume of carbon dioxide reduced in a given time.

Q_2 = volume of carbon dioxide supplied in that time.

It is found that the calculated R values increased rapidly to a maximum within one or two minutes from the start, and begin to decrease rapidly after 10 minutes to a constant value which remains almost unchanged. This value is taken as the reactivity of the carbon under test.

1.2.3. Critical air blast (C.A.B.) method.[17] This method uses an apparatus developed by the Northern Coke Research Committee in which is kept a bed of closely graded coke (14 - 25 B.S.S.) which is 25 mm deep and 40 mm in diameter. A measured rate of air (ft^3/min.) is then passed through the bed from the top to keep the bed in combustion state. The minimum rate of air which will keep the bed in that state is measured as the C.A.B. value. The lower the C.A.B. value, the higher the reactivity of the coke or coal. This method has been widely used in Britain for industrial purposes.

1.2.4. Modified ignition method.[18] This method is based on the gasification of a coke with air or oxygen. The rate of evolution of heat is the measure of the reactivity of the coke.

This method was developed by the Coal Research Laboratory, Pittsburg, U.S.A.

1.3. Physical properties influencing carbon reactivity.

Factors such as particle size and surface area, porosity, particle strength and crystalline structure are all known to have marked effects on the reactivity of carbon

as it is found in coke. It is well realised that uniformity of size of fuel in a gas producer, since it promotes uniform gas flow across the fuel bed, will ensure high volumetric efficiency and constancy of outlet gas composition. The principal regions in which reactions occur in gasification processes are at the coke surface and in the interstices between the coke pieces constituting the bed, and thus the nature and availability of coke surface as well as the chemical reactions and their rates at this surface will determine the overall reaction rate. The overall surface area of the coke or char is, of course, dependent on the size and shape of the pores contained in the solid particles. The narrower pores react faster as they provide larger surface area per unit volume.[19] Porosity, reactivity, and strength of coke are not independent factors but inter-dependent.

The physical structure of different types of carbon depends both on the method of preparation and on the carbon containing raw material. Thus great differences in reactivity are possible. The proportion of crystallographically dis-organized material may influence the reactivity by providing "active" or reaction sites. These active centres may be identified with the unsaturated edge atoms of the exposed graphite crystallites of carbon[79] or with the disordered

carbon atoms associated with the structure[20] and exist only at moderate temperatures. They are eliminated by thermal annealing at high temperatures.[21] Amorphous carbons prepared at low temperatures are highly reactive due to the presence of these active centres which exist to a lesser extent in graphitic carbons due to the high temperature involved in their preparation. Hence the reactivity of graphite carbons decreases with increase in degree of graphitization.

An extremely reactive type is carbon that is deposited on a porous carrier. Such carbon deposits often form on catalysts that are exposed to hydrocarbons or carbon monoxide. This has been demonstrated by Gilliland and his co-workers,[34] who deposited carbon at low temperatures (700 - 1100°F) on a reduced Nickel catalyst by the thermal cracking of hydrocarbons and studied the carbon reactivity. It was found that the carbon deposited from butane and carbon monoxide at 900°F was 10 times more reactive than that obtained from methane. The reactivity of carbon deposited from methane at 1400°F was found to be 10 times greater in reaction with carbon dioxide than with hydrogen.

1.4. Types of carbon available in gasification.

For a long time, coke was the sole raw material for gasification. However, capital, maintenance and labour costs for carbonising plant have increased together with the increase in price of carbonising coal. Thus low grade

coal has assumed an importance as a source of carbon for gasification. As the best types of coking coals are being preserved for metallurgical purposes, lower and lower grades of solid fuels are now being considered for gasification. These include, anthracite or anthracite fines or' breezes, deep-mined or open-cast low grade bituminous coals, high ash and high moisture content brown coals, lignites and peat, high moisture content wood or cellulosic material, heavy fuel oil with high sulphur content, light petroleum distillate and natural gas.

1.5. Synthesis gas production and its value.

"Synthesis gas" is essentially a mixture of hydrogen and carbon monoxide and now usually manufactured on an industrial scale either by gasification of a solid carbonaceous fuel, by the gasification of a liquid hydrocarbon fuel, or by the reforming of gaseous hydrocarbons such as natural gas. Some carbon dioxide is generally also present in the gas and the ratio of hydrogen to carbon monoxide can be varied by re-converting some of the carbon monoxide by reaction with steam.

$$CO + H_2O = CO_2 + H_2$$

Development of synthesis gas processes, as of any other manufacturing process, are closely related to economic trends. As a result the orientation of research in gasification has differed from country to country according to the nature of the indigenous fuel resources and national requirements.

One reason for its production which is applicable to all countries, is the utilisation of the low-grade fuels to produce cheaply synthetic liquid fuel or other vital chemicals. By nature all countries are not equally endowed with enough fuel resources. The world's petroleum, coal or gas fields are not systematically distributed to all the countries but situated within the borders of a few countries. Others have to depend on them for their day to day supply. There is no sure guarantee of their flow. It can stop at any time for political or other reasons, as happened to Germany during the last world war. Thus countries having only solid fuel resources will necessarily develop methods to utilise their indigenous fuel to produce liquid or gaseous fuels. For the countries rich in liquid fuel, other reasons apply. Although the present reserves of petroleum are quite high and should continue for another half-a-century, it must be recognised that the actual reserves are finite and will eventually be exhausted. Even if the day of declining production is still far away, there can be no doubt that the cost of production will inevitably show a general upward trend. The major factors in this cost trend will be the exploitation of relatively deep producing formations and off-shore drillings. This inevitable rise in the cost of recovering petroleum will in the end justify the production of synthetic fuel from synthesis gas utilising other low grade fuel.

There are many chemicals in the market today which were earlier costly, but are now produced cheaply from synthesis gas. Hence attempts are being made to devise ways to make as cheap a gas as possible which will not only open the field to more chemical manufacture from synthesis gas but to synthetic liquid fuel also.

Synthesis gas can be used as a starting material for the production of various liquid and gaseous hydrocarbons, chemicals and hydrogen for hydrogenation industries. The various processes that can utilise synthesis gas include production of:

(a) liquid hydrocarbons by Fischer-Tropsch synthesis,

(b) methane or synthetic high-Btu pipeline gas by methanation,

(c) methanol and higher alcohols directly,

(d) higher alcohols by reduction with olefins in OXO - synthesis,

(e) hydrogen for use in the hydrogenation of coal to produce either liquid fuels and by-products or gaseous hydrocarbons and for use in the synthesis of ammonia,

(f) hydrogen or hydrogen-rich gas mixtures for the direct reduction of iron ore.

1.6. <u>The potential of natural gas.</u>

Natural gas is found in large reservoirs under the surface of the earth in a "dry" condition, and also with

petroleum in oil-wells in a "wet" condition. Gas associated with petroleum may be recovered in the oil-refinery by suitable separation plant. Almost all the oil-producing countries have vast reserves of natural gas. A small portion of these gases are recycled to the oil-well for pressurisation, but a considerable proportion is burned due to lack of economic outlets. It is reported that in middle eastern countries about 1,000 million ft^3 of gas is daily wasted in this way.[22]

Natural gas also exists in some coal pits. This presents a hazard and modern drainage schemes are employed to recover quite a large amount of the gas. It is burned at the pit-head to raise steam or piped to local gas undertakings for enriching towns gas or for reforming.

Dry deposits of natural gas exist in several countries; U.S.A., U.S.S.R., Canada, Algeria, Netherland, and Pakistan have large reserves of dry gases. Smaller reserves have also been found in France and Italy. The total reserves of natural gas, both dry and wet (including the latest estimate for Netherland and Canada[23,24]), are estimated to be 790 trillion cubic feet.[25]

The vast reserve of Slochteren in Netherland is so close to the North Sea that it has brought a spate of activity by the big oil companies of the world to find gas in this sea-bed.[23]

1.7. The manufacture of synthesis gas from natural gas.

There are two commonly used methods for synthesis gas manufacture from natural gas. These are:-

(a) a catalytic steam-reforming process developed by the standard oil company of New Jersey,

(b) a partial oxidation process developed by the Texaco Oil Co.

1.7.1. Catalytic steam-reforming.[26,27] In this process, a mixture of gas and steam is introduced into a reforming furnace kept at 1300 - 1500°F, and in which is suspended a multiplicity of heat resisting steel tubes of varying diameters and wall thickness. These contain uniformly sized particles of a highly active nickel catalyst. The reforming of the gas proceeds according to the following reaction

$$CH_4 + H_2O = CO + 3\ H_2.$$

This reaction is endothermic and hence greatly favoured by high temperature and low-pressure. To overcome, however, the compression cost of the product gases, the process is operated at elevated pressures which shifts the equilibrium towards methane formation. To counteract this a high temperature is maintained inside the furnace. This has been possible by improved furnace design and improved heat transfer through the packed bed. This process is now widely used for the provision of gas for ammonia and methanol synthesis.

1.7.2. Partial oxidation process.[28] In this process, methane is burnt non-catalytically in a specially designed burner with a limited supply of oxygen under pressure. The first reaction of methane with oxygen is

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$

and then a series of reactions follow between the product gases and methane

$$CH_4 + CO_2 = 2\ CO + 2\ H_2$$
$$CH_4 + H_2O = CO + 3\ H_2$$
$$CO + H_2O = CO_2 + H_2$$
$$2\ CO = CO_2 + C$$

But the overall reaction may be depicted as

$$CH_4 + \tfrac{1}{2}\ O_2 = CO + 2\ H_2$$

The outlet gas is obtained under pressure thus saving the cost of compression. This process is also increasingly used for ammonia synthesis.

1.7.3. Limitations of the above processes. It is well-known that water-gas formation is favoured by high temperature and low-pressure and that methane formation is favoured by low-temperature and elevated pressure. Thus the steam-reforming process carried out at elevated pressure to save compression costs is limited by temperature. Due to the presence of substantial amount of unreformed methane in the

product gas, a second reformer is necessary. The process is moreover limited by the steam : methane ratio. A steam : methane ratio of 2 mol/mol is considered to be the minimum to avoid carbon deposition on the catalyst.[27] The partial oxidation process is also limited by the oxygen : hydrocarbon ratio. This is considered to be very critical and hence accurate control is necessary to provide steady reaction conditions.[28] The cost of production of synthesis gas by these processes prevents them from being suitable for synthetic liquid fuel production.

1.7.4. Requirements of an ideal process and the reactions involved.

An ideal process for the manufacture of synthesis gas should be flexible in terms of product gas composition. The hydrogen : carbon monoxide ratios required by various processes are different, and a process for synthesis gas might be called upon to meet the requirements of several such processes. As the processes for synthetic chemicals have distinct boundaries for their needs for efficient operation, so also a synthesis gas process has its own fixed process conditions which cannot be changed without incurring loss in efficiency. A specific example of the varied requirements of a process is the Fischer-Tropsch synthesis process whose synthesis gas requirement varies in volume and composition according to the catalyst and the pressure, temperature and time of contact selected to yield

a primary product with desired amount of saturated to unsaturated hydrocarbons. Synthesis gas made in a single step will have difficulty in meeting such varied requirements, and can only be met by employing several production steps.

With such a situation, it seems that a process which can manufacture the two synthesis gas components, viz. carbon monoxide and hydrogen, separately from a single feed material such as natural gas is worthy of consideration. Such a process could well utilise the two reactions:-

(a) decomposition of methane into its elements carbon and hydrogen,

$$CH_4 = C + 2\ H_2$$

(b) gasification of the deposited carbon to produce carbon monoxide,

$$C + CO_2 = 2\ CO$$

It is envisaged that the process would be a cyclic one in which a reactor produced alternately hydrogen and carbon monoxide. By the use of two such reactors in parallel and suitable gas valve arrangements it might be possible to obtain virtually continuous flows of both product gases.

1.8. Purpose of research.

The evolution of a suitable process for the manufacture of synthesis gas by the above scheme requires a detailed study of both reactions and the influence of catalysts on their rates. As will be described later, substantial methane

decomposition can be achieved at moderate temperatures over freshly reduced iron powder. A considerable amount of work has been carried out on this reaction by Van Vormer[36] and it was not proposed to continue this study here. However, in the course of burning off carbon deposited on the iron powder, isolated measurements of the analysis of the gas coming from Van Vormer's reactor showed exceptionally high values for carbon monoxide. This point was later noted and studied further by Gibb et al[29] who in fact showed that the concentration of carbon monoxide coming from such a unit appeared to exceed that predicted by the Boudouard equilibrium. It appeared therefore worthwhile to make a systematic study of the reaction

$$C + CO_2 = 2\ CO$$

under conditions that would apply to such a process of manufacturing hydrogen and carbon monoxide separately for better mixing as synthesis gas. With a suitable and cheap catalyst such as iron and a moderate temperature of operation, i.e. 1000 - 1300°F, such a two-staged process could well have commercial attraction in the event of large amounts of cheap methane becoming available in the United Kingdom.

It was hoped also to make calculations of free energy for the seemingly very reactive carbon and to determine how the reactivity was related to the iron substrate. To ensure constant temperature conditions, it was hoped to carry out most of the experiments in a fluidized bed reactor.

1.9. Theory of methane decomposition.

1.9.1. Thermodynamics. Methane is a stable gas and complete decomposition into its elements takes place at well above 1000°C[15,30,31]. It is an endothermic process and hence temperature dependent. The degree of decomposition increases with increasing temperature and its rate is strongly affected by the surface area of porous materials[31-33] and catalysts which accelerate it considerably[34-37]. The thermodynamic equilibrium of the system ($C - H_2 - CH_4$) has been studied extensively by several authors[32,37-43] at high temperature and high pressure,[42-43] at high temperature and low pressure (atmospheric)[32,37-40] and at low temperature and low pressure[39,41]. The general conclusions drawn from these studies was that low temperature and high pressure favour methane formation and high temperature and low pressure favours its decomposition. The effect of temperature on the thermodynamic equilibrium of the system, ($C - H_2 - CH_4$) is shown in Figure 1.1. These data were taken from the "Thermodynamics of gasification and gas-synthesis reactions" by Lavrov, Korovov, and Piliphova[44] in preference to that of Rossini et al[48,50] because the former compilation is the most modern one and is based on spectroscopic data.

1.9.2. Kinetics and catalysts. The decomposition of methane was first investigated comprehensively by Berthelot[45] while studying the decomposition of hydrocarbons at high temperatures. He maintained that methane is not directly

decomposed into its elements, carbon and hydrogen, but produces intermediate compounds, like acetylene or ethane, which subsequently decomposes into carbon and hydrogen. The possible reactions for this explanation are

$$2\ CH_4 = C_2H_2 + 3\ H_2$$

$$2\ CH_4 = C_2H_6 + H_2$$

This view was strongly refuted by Bone and Coward.[31] Working in the temperature range of 1150 - 1160°C, they found no evidence of acetylene formation and concluded that methane was directly decomposed into its elements. They showed that methane decomposition is a first order reaction and that the rate of decomposition is greatly influenced by temperature and the presence of porous materials.

However, the true mechanism of methane decomposition still remains debatable. The modern process of acetylene manufacture from methane lends support to the Berthelot theory to some extent. The present process employs a fast quenching step for the product gases of methane decomposition where the acetylene fraction ranges from 8% to 20%. The thermal conversion of methane may well be represented by the following reactions

$$2\ CH_4 = C_2H_4 + 2\ H_2$$

$$2\ CH_4 = C_2H_2 + 3\ H_2$$

It has been found that the percentage of acetylene increases in the product gases as the temperature at which the methane

is decomposed increases (from 6.8% at 100°C to 18.2% at 1200°C).[46] The most significant studies of methane decomposition were carried out by Gilliland and Harriot[34], Boynton[35] and Van Wormer.[36] Gilliland and his co-workers, in order to study the reactivity of deposited coke, decomposed methane over reduced nickel in a fluidized bed within a temperature range of 700 - 1100°F and studied the rate of carbon deposition (which is indirectly the rate of methane decomposition) and found that the rate decreases linearly with increasing carbon on the bed, due to the coverage of the more active sites of the catalyst by carbon. They calculated the apparent activation energy of methane decomposition to be 23 Kcal per.g.mole. Boynton[30] and Van Wormer[31] while studying the reduction of iron ore with methane in a fluidized bed found that the increasing methane disappearance with increasing metallic iron in the bed was due to the catalytic decomposition of methane by reduced iron. Based on their experimental findings they proposed the following rate equation for methane decomposition.

$$R_m = k_{Fe}\, p_m\, W_{Fe}$$

where

R_m = rate of methane decomposition

k_{Fe} = specific reaction rate constant for metallic iron

p_m = methane partial pressure in the gas phase

W_{Fe} = total weight of metallic iron in the bed.

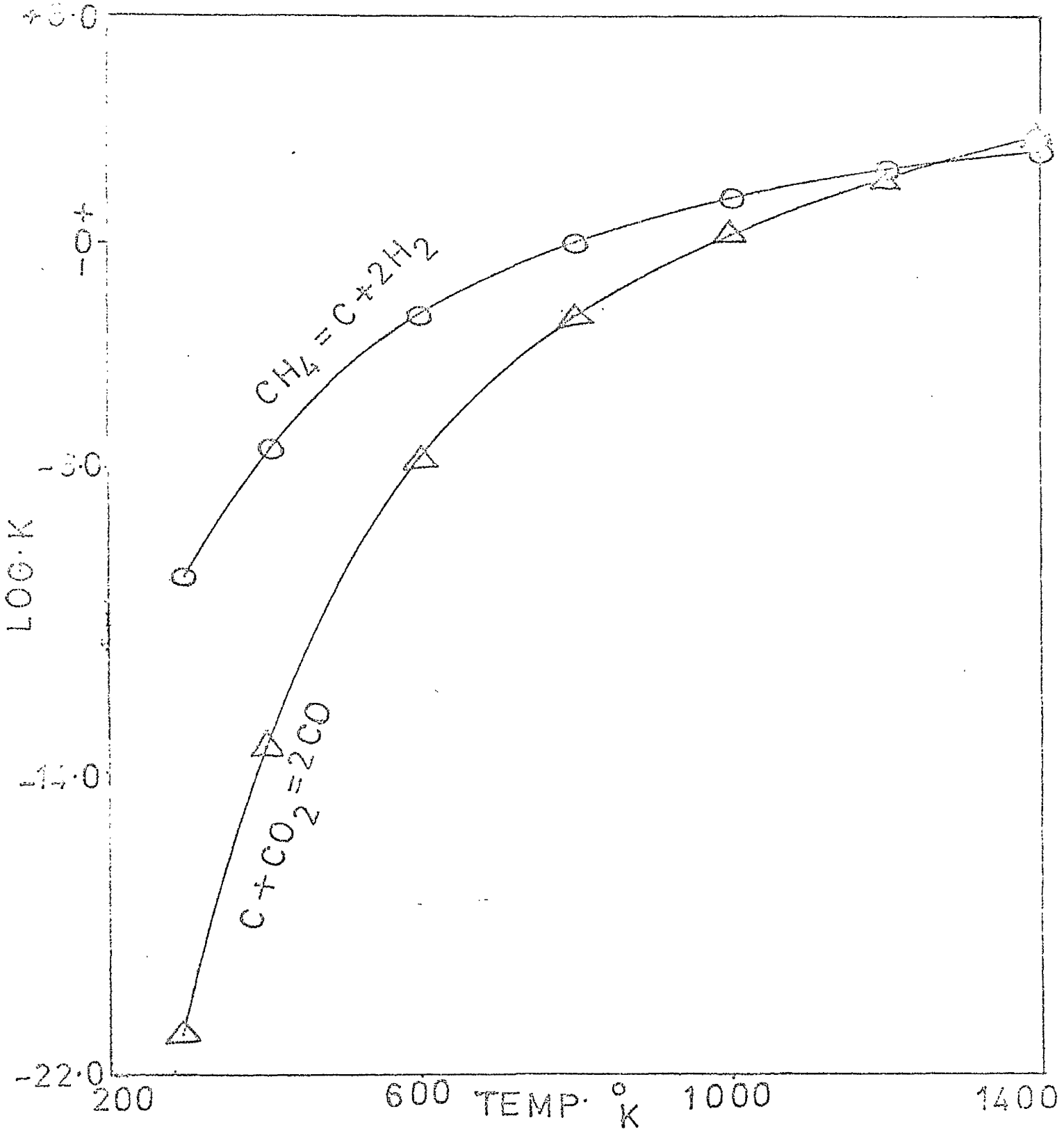
They showed that hydrogen-reduced iron has high activity which decreases rapidly to an asymptotic value with increasing time of exposure to methane and accompanying carbon accumulation. Iron containing substantial carbon conforms to the conventional Arrhenoous equation confirming the conclusions that reaction rate is controlling and methane deposited carbon has negligible diffusional resistance.

1.10. Theory of Boudouard reaction.

1.10.1. Thermodynamics. This reaction which occurs in the reducing zone of a gas producer is represented by the equation :-

$$C + CO_2 = 2\ CO$$

It is an endothermic reaction and hence thermodynamically carbon monoxide formation is favoured by high temperature and low pressure. The effect of temperature on the thermodynamic equilibrium of this reaction was first studied by Boudouard[47], after whom the reaction is named, and subsequently by Rhead and Wheeler[48] at various temperatures. The first comprehensive compilation of the equilibrium constants at different temperatures for this reaction was made by Rossini and his co-workers[49]. They calculated the equilibrium constants based on the thermodynamic data of the gases. Gumz[50] developed an equation for the equilibrium constant of this reaction based on the calculated values of Rossini et al. By this equation, equilibrium constant for any temperature from 700°K to 1500°K



FIG·1·1

could be calculated. The values calculated by Rossini and co-workers were later recalculated using up-to-date physical constants but this incurred no significant modification of their earlier values for the equilibrium constants.[51,52] A recent compilation of these thermodynamic constants based on spectroscopic data of gases has been made by Lavrov, Korolov and Piliphova[44] which are claimed to be much more reliable than Rossini's. These latest equilibrium data were used throughout this work. The effect of temperature on the equilibrium of the Boudouard reaction is shown in Figure 1.1.

1.10.2. Kinetics and catalysts. Extensive studies have been made of this reaction by a number of authors[1-14,41,42,53-86] both to determine the reactivity of different carbon species and to understand the mechanism of the reaction. This is a heterogeneous reaction and very complex in nature. Many routes have been proposed for the most probable mechanism but no one route has met with general approval. There is, however, agreement that the reaction proceeds through the formation of a surface oxide and the rate of decomposition of this surface oxide is the rate controlling factor. Two possible mechanisms[75] are discussed below:-

Mechanism A: This mechanism which is supported by most of the authors[55,59,61,68,70,73,74] on the basis of radioactive tracer and kinetic studies consists of two steps:

The first step is a reversible oxygen surface reaction as shown by the equation

$$C_f + CO_2 = C(O) + CO$$

where C_f denotes an active carbon free - site capable of reaction and C(O) represents chemisorbed atomic oxygen.

The second step is a unidirectional decomposition or gasification as follows :-

$$C(O) = CO + nC_f$$

where nc_f denotes that on average n active centres must be produced for each carbon atom gasified.

Mechanism B: This mechanism was proposed by Gadsby and co-workers[57] based on their experimental findings. The following steps comprise the mechanism.

Firstly, a unidirectional oxygen exchange at the surface

$$C_f + CO_2 = C(O) + CO$$

then a reversible chemisorption of carbon monoxide upon free-sites

$$C_f + CO = (CO) \text{ adsorbed}$$

followed by a unidirectional gasification of surface oxide

$$C(O) = CO + nC_f$$

and in the presence of thermal annealing

$$C_f = C \text{ (inactive)}$$

Gadsby and co-workers proposed this mechanism based on the results of charcoal chemisorption at 750°C and at

zero to 400 mm Hg total pressure which indicated that wide variation in carbon dioxide partial pressures corresponded more closely to variation in carbon monoxide partial pressure than to changes in amount of oxygen complex absorbed. In addition, the quantity of oxygen complex remained relatively constant with variation in carbon monoxide partial pressure at constant carbon dioxide partial pressure. This was taken as evidence that the rate inhibition must have been due to carbon monoxide chemisorption and not to the reverse oxygen exchange as postulated in the first step of mechanism A.

The above proposition of Gadsby and co-workers was strongly refuted by Reif[61] on the basis of kinetic studies. It was argued that the activation energy of the first step of mechanism A as calculated by Gadsby and co-workers was in error due to the negative sign (- 16.8 kcal) which was not in accord with the positive values of other studies which support the thermodynamic feasibility of the first step in mechanism A.

There is, however, general agreement[57.58.61] that the rate of carbon gasification by carbon dioxide fits a Langmuir type of equation as

$$R_{co_2} = \frac{kp_{co_2}}{1 + ap_{co} + bp_{co_2}}$$

where k, a and b are functions of one or more of the rate constants and p_{CO_2} and p_{CO} are the partial pressures of carbon dioxide and carbon monoxide. This equation is consistent with the proposed mechanism A. It states that the kinetics of the reaction will be first order with respect to carbon dioxide if $ap_{CO} \ll 1$ and $bp_{CO_2} \ll 1$, i.e. at low carbon dioxide concentration and low temperature. Zero order kinetics is indicated if $ap_{CO} \ll 1$ and $bp_{CO_2} \gg 1$, which is fulfilled at low temperature and high carbon dioxide partial pressure. It has been demonstrated that the constants a and b decrease with temperature,[57,58] therefore at high temperatures and high pressures, the inequalities $ap_{CO} \gg 1$ and $bp_{CO_2} \gg 1$ still hold, resulting in a first order reaction. Thus orders of reaction varying from zero to unity are possible. This has been confirmed by several authors.[66,68,71]

Blakeley[66], Vulis and Vitman[72], and Sawai and co-workers[76] confirmed that the over-all reaction rate of the carbon - carbon dioxide reaction is controlled by chemical reaction at the carbon surface up to about 1100°C. Above 1500°C it is controlled by diffusion. At low temperature, the reaction between carbon and a gasifying medium is controlled by the chemical resistance of the carbon surface and the gas velocity has no effect on the reaction rate. As temperature is increased, the chemical

resistance at the surface decreases and the effect of diffusional resistance increases and at higher temperatures, the chemical resistance is overshadowed by diffusional resistance. The reaction rate is then controlled by gas velocity and the partial pressure of the gasifying medium.

The activation energy of this reaction has been variously reported.[2,65,74,77-80] The wide range in values given may be ascribed to :-

(a) varying degree in mass-transport,

(b) the influence of impurities, and

(c) the percentage carbon burn-off.[15]

The production of carbon monoxide has been shown to be greatly accelerated by the presence of a catalyst.[29,36,54,81-86] Catalysts found to be active are Nickel,[81] Na_2CO_3,[54,81-85] and Fe.[29,36,86] They appear to help in the faster removal of the surface oxide formed on the carbon.

The evidence of carbon monoxide poisoning of the reaction came from Hinshelwood and his associates[56] and is supported by Gilliland and his associates.[58] Hinshelwood found that the gasification rate was greatly retarded when carbon monoxide was introduced along with carbon dioxide in a carbon gasification experiment.

1.11. Quasi-equilibria and carbon free energy.

If chemical reactants are left in adequate contact for an infinite length of time the extent to which reaction takes place is limited by the chemical thermodynamic equilibrium of

the system. In a flow system, if equilibrium is reached before the gases leave the reactor, the outlet composition of these gases will be calculable from the known thermodynamic data. The equilibrium constant for a reaction is related to the free energy change by the equation

$$\Delta F = - RT_1 \ln K$$

where the symbols have the usual significance and the standard state for reference has been defined.

Recent consideration of gas analyses from fluid bed gasifiers by Squires[43] appear to indicate that in certain cases equilibria may be exceeded. The outlet gas composition would appear to suggest that the extent of reaction has gone beyond that which should be thermodynamically possible. Thus he shows that reactive chars in fluidized - beds may yield methane concentration substantially in excess of that predicted by the β-graphite-hydrogen equilibrium for the reaction

$$C + 2\ H_2 = CH_4$$

It may be said, of course, that such data represent a quasi-equilibrium over very active forms of carbon and as such should not be compared directly with β-graphite. Using the later equilibrium as a yardstick, however, one is able to calculate the seemingly excess of free energy for such chars over that of β-graphite and thus obtain a scale of

carbon activity. The data reviewed by Squires indicates a possible excess of free energy for such forms of carbon at 1700°F ranging from 1800 cal/g.mole to 4800 cal/g.mole. Such excessive free energies must be associated with the difference between the thermal properties of the bulk solids and finely divided solids of high surface area per unit weight. It is extremely difficult also to allow adequately for the activating effects of adsorbed hydrogen on such carbon surfaces. Moreover, when the carbon is deposited as a thin film on an active catalyst surface, the apparent carbon reactivity may be expected to differ considerably from that of bulk graphite. This was in fact shown to be the case for carbon deposited on Nickel by Gilliland and Harriot[34]. The data furnished by Gibb et al[29] suggest that iron has the same influence.

2. PRELIMINARY FIXED-BED STUDIES

The ultimate object, as stated in the introduction was to study the Boudouard equilibrium in a fluidized bed for carbon deposited on a catalyst. As a basis for comparison and in order to become familiar with the experimental results to be expected, a number of experiments were carried out on a fixed bed of metallurgical coke. The effects of temperature, coke particle size, gas flowrate and general arrangement of the bed on the outlet gas analysis were all studied.

Experiments were carried out also on carbon deposited in a fixed bed of reduced iron particles.

2.1. Preparation of coke powder and iron catalyst.

A consignment of 3/4 inch screened metallurgical coke was obtained from the coke ovens associated with a local iron works. It had been prepared by the carbonization of a blend of Scottish coking coals. The swelling index of the blend as determined by B.S.1016: part 12, 1959, was 5.5. A representative sample of the coke was ground to pass 72 mesh B.S.S. The proximate analysis of the powder was then determined by the methods set out in B.S.1016: part 4, 1957. The results were as indicated in Table 2.1 below.

TABLE 2.1

	%
Moisture	1.20
Ash	11.20
Volatile matter	0.62
Fixed carbon	86.98
	100.00

The main bulk of the coke was then passed through a series of laboratory crushing and grinding units, viz. jaw-crusher, roll-mill and hammer-mill. The fine powder was then graded into a number of suitable sieve-size ranges by means of British Standard sieves and a mechanical (Rotap) sieve shaking machine. The size ranges selected for gasification studies were

- 16 + 18 mesh	- 60 + 72 mesh
- 22 + 25 "	- 72 + 100 "
- 44 + 60 "	- 100 + 150 "

A supply of iron ore was obtained also from a local iron works. The ore was a Cerro Bolivar haematite from South America. The iron content of this ore was reported to be 56% (i.e. 80% Fe_2O_3) and 20% silica and other gangue constituents. As supplied, the ore was in the form of 1 to 4 inch lumps. The larger pieces were broken in the laboratory jaw-crusher and then all the ore was crushed in the laboratory roll and hammer mill. The powdered ore was then graded into a number of size ranges by B.S. sieves.

The size ranges- 16 + 18 mesh and - 50 + 100 mesh were retained for use in the gasification studies. The former was used in fixed bed studies and the latter for fluidisation experiments.

Screen analysis of the - 52 + 100 mesh fraction was determined by the method laid down in B.S. 1796 : 1952. The results were as given in Table 2.2.

TABLE 2.2

	wt. per cent
Through 52 mesh B.S.S. and on 60 mesh B.S.S.	18.94
" 60 " " 72 "	21.35
" 72 " " 100 "	48.75
" 100 " " 120 "	9.47
" 120 " " 150 "	1.36
" 150 " "	0.13
	100.00

2.2. Fixed-Bed Gasification Apparatus.

This part of the work was undertaken on a simple apparatus consisting of the following parts.

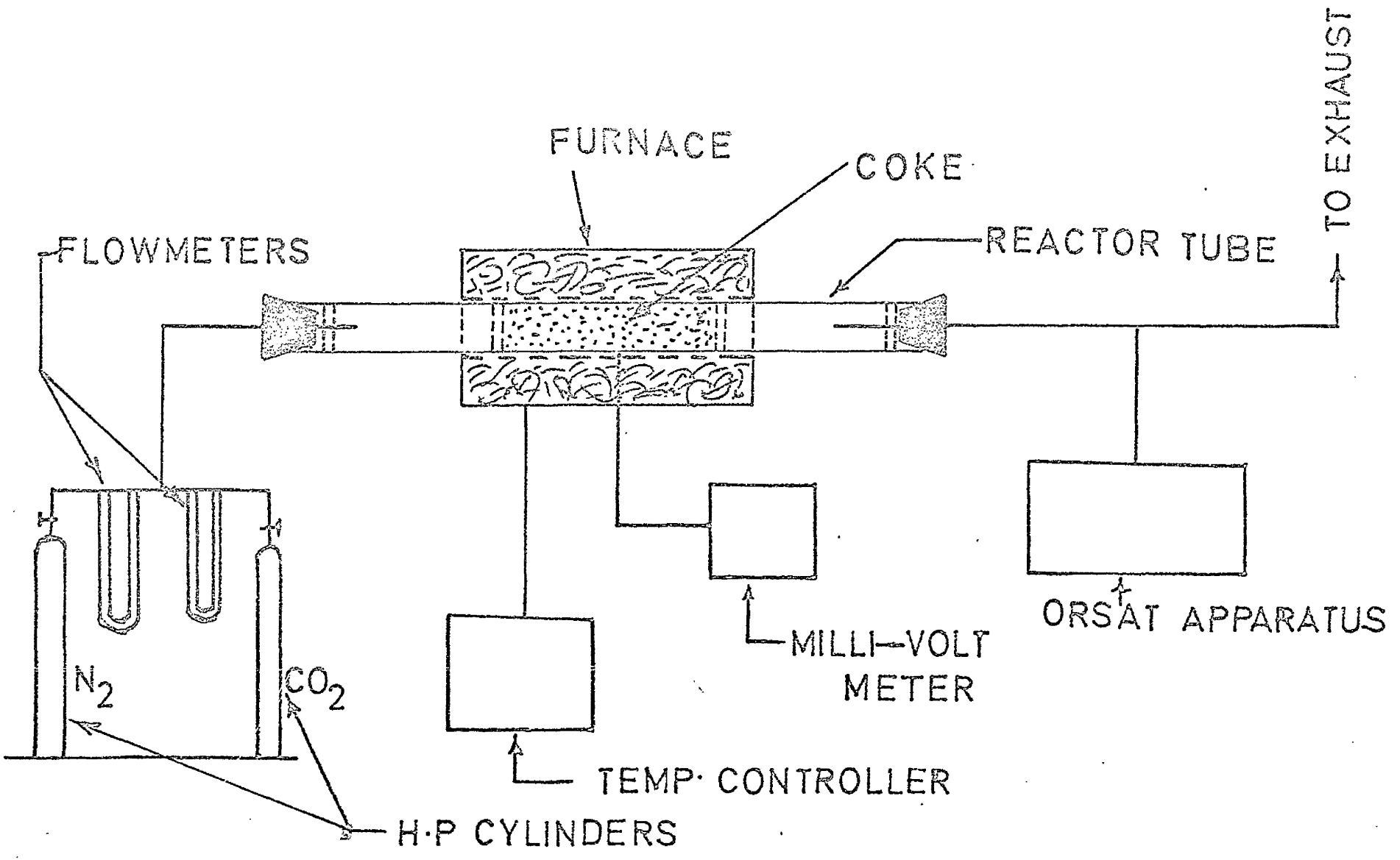
(a) Furnace

(b) Reaction tube

(c) Gas metering instrument, and

(d) Gas analysis apparatus.

A flow-sheet of the general arrangement is shown in Figure 2.1.



FLOW SHEET
FIG. 2.1

2.2.1. Furnace. This was an electrical high temperature tube furnace capable of operating up to 1400°C. It could accommodate a $1^1/4$ inch O.D. refractory furnace tube and heat a length of 13.5 inches. Heating was by direct radiation from carbon resistance rods which were grouped around the furnace tube. Furnace temperature control was provided and the furnace temperature was measured by a Chromel-Alumel thermocouple placed near to the outer surface of the furnace tube at the mid-point of its length, and indicated by a temperature calibrated millivoltmeter. The furnace could be arranged so that the furnace tube axis was horizontal or vertical.

2.2.2. Reaction tube. This was a Mullite tube 30 inches long and with an internal diameter of 0.9 inch. Two neoprene rubber stoppers held the inlet and outlet gas-lines in place. They were protected from direct radiation from the reactor bed of the furnace by 1/4 inch thick discs of soft asbestos sheet placed in the tube before them.

2.2.3. Gas metering. This was achieved by manometric flowmeters filled with concentrated sulphuric acid and previously calibrated against a standard wet gas-meter for each individual gas in use. Two such flowmeters were used in these experiments, one for nitrogen and another for carbon dioxide.

2.2.4. Gas analysis apparatus. This was a British Standard Orsat apparatus permitting analysis for carbon dioxide, oxygen and carbon monoxide. Nitrogen was determined by difference.

2.3. Experimental Procedure.

A weighed amount of coke of a particular particle-size range was taken which would give a packed bed length in the tube of 12 cms. The coke was held in place inside the reaction tube by 1 inch thick plugs of asbestos wool at each end. Initially the furnace was used with the reaction tube lying in a horizontal position in it. Nitrogen was continuously passed through the tube, and the temperature raised to the desired value by adjustment of the electrical controls. When the desired temperature had been reached, carbon dioxide was introduced into the reactor at the required rate with the nitrogen. The exit gases were then analysed by Orsat at suitable time intervals. This experiment was repeated at different temperatures, flowrates and coke particle sizes. A new series of experiments was then carried out with the reaction tube vertical.

The complete series of experiments were as follows :-

(a) With reaction tube horizontal:

(i) effect of temperature,
(ii) effect of flowrate,
(iii) effect of particle size range.

(b) With reaction tube vertical and gas flowing upward:

(i) effect of flowrate,
(ii) effect of particle size range.

In the case of the later experiments, the bed was supported by a perforated stainless steel disc which was in turn supported by a steel spiral pushed inside the reactor from below.

2.4. Evaluation of "Equilibrium Ratio".

Although it was realised that the time of contact of carbon dioxide with coke in the reaction tube was very likely to be insufficient for chemical equilibrium to be reached, it was decided to evaluate an "equilibrium ratio" for the exit gases in the manner normally used to calculate an equilibrium constant. The value obtained when compared with the constant at the same temperature for the Boudouard equilibrium would give a measure of the proximity to equilibrium.

The most convenient way of representing the equation for the calculation of equilibrium constant is in terms of partial pressures. For the Boudouard equilibrium, this is as follows :-

$$K = \frac{p^2_{CO}}{p_{CO_2}}$$

where p_{CO} and p_{CO_2} are partial pressures of carbon monoxide and carbon dioxide. This equation can also be written in terms of fractional volumes of each gas

$$\frac{p^2_{CO}}{p_{CO_2}} = \frac{(v_{CO})^2 p^2}{(v_{CO_2})p} = \frac{(v_{CO})^2 p}{v_{CO_2}}$$

For reaction at atmospheric pressure (p = 1), the equation becomes

$$K = \frac{(v_{CO})^2}{v_{CO_2}}$$

This equation was used to calculate the equilibrium ratios in the above experiments.

2.5. Calculation of residence time.

The residence time of a flowing fluid in passing through an empty vessel largely depends on the flowrate of the fluid and the dimensions of the vessel. The calculation of residence time becomes a little more complicated if the vessel is packed with granular material. The velocity of the fluid within the vessel will depend on the available flow channels or bed voidage. A relationship to enable residence time to be calculated for a gas flowing through a bed of solid particles involves such parameters as gas flowrate, bed length and diameter, weight of the solid in the bed and the true density of the solid particles.

Hence, if

V = flowrate of the fluid, ft^3/min.

D_1 = diameter of the tube, ft.

L = length of the bed, ft.

W = weight of the solid bed, gms.

ρ = true density of the solid particles in the bed, gms/cm^3 or lbs/ft^3.

Then overall volume of the bed

$$= \frac{\pi}{4} D_1^2 L, \quad ft^3$$

Volume of the solid $= \frac{W}{\rho} ft^3$.

Volume of the free space in the bed

$$= \frac{\pi}{4} D_1^2 L - \frac{W}{\rho} ft^3.$$

Residence time $= \frac{1}{4V} \left(\pi D_1^2 L - \frac{4W}{\rho}\right)$ mins.

This equation was used to calculate the residence time of the flowing fluid inside the reactor.

2.6. Experimental Results.

2.6.1. Horizontal reaction tube. The results of the various experiments are tabulated below in Tables 2.3 to 2.5, and plotted in Figures 2.2 to 2.5.

TABLE 2.3 Effect of furnace temperature

Length of the bed of coke particles = 12 cms
Weight of coke bed = 22.8 gms.
Particle size range = - 16 + 18 mesh B.S.S.
Inlet gas flowrate = 1320 c.c/min. at 20°C
Inlet gas composition = 50.75% carbon dioxide
49.25% nitrogen

Run No	Sample taken at (min)	Temp. °C	Per cent in off-gas CO_2	Per cent in off-gas CO	K calculated	Log K calculated
1	0	900	-	-		
	10		50.1	1.60	0.51×10^{-3}	-3.29243
	30		50.2	1.50	0.447×10^{-3}	-3.34969
	60		50.2	1.50	0.447×10^{-3}	-3.34969
	90		50.3	1.50	0.446×10^{-3}	-3.35069
2	0	1100	-	-		
	10		40.0	17.2	7.39×10^{-2}	-1.13101
	30		40.6	16.0	6.305×10^{-2}	-1.20012
	60		41.2	15.0	5.461×10^{-2}	-1.26273
	90		41.8	14.0	4.688×10^{-2}	-1.32901
3	0	1300	-	-		
	10		16.6	46.4	1.2969	0.11263
	30		20.0	44.0	0.9680	-0.01412
	60		26.2	34.8	0.4622	-0.33517
	90		33.0	25.0	0.1894	-0.72261

TABLE 2.4 Effect of carbon dioxide flowrate

Length of the bed of coke particles = 12 cms.
Weight of the coke bed = 22.8 gms.
Particle size range = - 16 + 18 mesh B.S.S.
Temperature of gasification = 1100°C

Run No.	Sample taken at (min)	Flow rate c.c./min. N_2	Flow rate c.c./min. CO_2	Per cent off-gas CO_2	Per cent off-gas CO	K calculated	Log K calculated
1	0	605 (49.4%)	620 (50.6%)				
	5			42.0	10.0	2.3809×10^{-2}	-1.6234
	30			42.4	9.6	2.1735×10^{-2}	-1.66294
	60			43.4	8.6	1.7041×10^{-2}	-1.7685
	90			44.0	8.0	1.4545×10^{-2}	-1.83745
2	0	300 (49.4%)	308 (50.6%)				
	5			27.6	25.8	24.1173×10^{-2}	-0.61780
	30			31.2	19.6	12.3028×10^{-2}	-0.91009
	60			32.2	19.0	11.2111×10^{-2}	-0.95036
	90			33.2	18.0	9.7590×10^{-2}	-1.01060
	120			33.4	17.4	9.0646×10^{-2}	-1.04248
3	0	197 (48.4%)	210 (51.6%)				
	5			29.4	30.6	31.4889×10^{-2}	-0.49702
	30			30.6	26.4	22.7764×10^{-2}	-0.64262
	60			33.0	25.0	18.9393×10^{-2}	-0.72285
	90			34.0	24.0	16.94117×10^{-2}	-P.77107
4	0	101.5 (50.0%)	101.5 (50.0%)				
	5			18.4	43.6	103.3130×10^{-2}	0.01411
	30			22.4	37.6	63.4461×10^{-2}	-0.19764
	60			26.0	34.0	44.4615×10^{-2}	-0.35203
	90			27.4	31.6	36.4437×10^{-2}	-0.43842
	120			28.0	29.0	30.0357×10^{-2}	-0.52245

TABLE 2.5 Effect of particle size range

Length of the bed of coke particles = 12 cms.
Temperature of gasification = 1100°C
Inlet gas flowrate = 297 c.c./min. at 20°C
Inlet gas composition = 50.0% carbon dioxide and 50.0% nitrogen
Weight of the bed for -22+25 mesh range B.S.S. = 28.5 gms.
" " " -60+72 " " = 33.0 "
" " " -72+100 " " = 39.5 "

Run No.	Sample taken at(min)	Particle size range mesh B.S.S.	Per cent off-gas CO_2	CO	K calculated	Log K
1	0	-22+25	-	-		
	5		27.4	31.6	36.3708×10^{-2}	-0.43926
	30		27.6	30.6	33.9260×10^{-2}	-0.46954
	60		28.0	29.0	30.0357×10^{-2}	-0.52245
	90		28.0	28.0	28.0000×10^{-2}	-0.55284
	120		28.0	28.0	28.0000×10^{-2}	-0.55284
2	0	-60+72	-	-		
	5		29.0	30.4	31.8675×10^{-2}	-0.49674
	30		27.6	31.4	35.7231×10^{-2}	-0.44709
	60		27.2	31.4	36.2485×10^{-2}	-0.44081
	90		26.8	31.6	37.2597×10^{-2}	-0.42888
	120		26.2	31.8	38.5969×10^{-2}	-0.41352
3	0	-72+100	-	-		
	5		26.6	32.4	39.4646×10^{-2}	-0.40274
	30		23.4	37.6	60.4170×10^{-2}	-0.21889
	60		22.8	37.6	62.0070×10^{-2}	-0.20761
	90		22.6	37.8	63.2230×10^{-2}	-0.19908
	120		21.0	38.0	68.7619×10^{-2}	-0.16266

TABLE 2.6 Effect of using carbon dioxide only

Length of the bed of coke particles = 12 cms.
Weight of the bed of coke = 38.5 gms.
Particle size range = -72+100 mesh B.S.S.
Temperature of gasification = 1100°C
Inlet flowrate of carbon dioxide = 148.5 c.c/min. at 20°C

Run No.	Sample taken at(min)	Per cent off-gas CO_2	CO	K calculated	Log K calculated
	0	-	-		
	5	41.4	58.6	82.9458×10^{-2}	-0.08124
1	30	36.0	64.0	113.7777×10^{-2}	+0.05578
	60	31.4	68.6	149.8713×10^{-2}	+0.17555
	90	30.0	70.0	163.3333×10^{-2}	+0.21299
	120	29.0	71.0	173.8275×10^{-2}	+0.24006

2.6.2. Vertical Reaction Tube. With the tube vertical, the inlet gas was passed through the bed of coke in an upward direction.

TABLE 2.7 Effect of carbon dioxide flowrate

Length of the bed of coke particles = 12 cms.
Weight of the bed of coke = 22.8 gms.
Particle size range = -16+18 mesh B.S.S.
Temperature of gasification = 1100°C

Run No.	Sample taken at(min)	Flowrate c.c/min. N_2	Flowrate c.c/min. CO_2	Per cent off-gas CO_2	Per cent off-gas CO	K calculated	Log K
1	0	99.25 (50.0%)	99.25 (50.0%)	-	-		
	5			25.4	35.1	48.5043×10^{-2}	-0.31426
	30			25.6	35.0	47.8515×10^{-2}	-0.32010
	60			25.8	34.2	45.3348×10^{-2}	-0.34361
	90			26.8	32.2	38.6880×10^{-2}	-0.41251
	120			27.0	32.0	37.9259×10^{-2}	-0.42113
	150			26.4	30.6	35.4681×10^{-2}	-0.45017
2	0	148.5 (50.0%)	148.5 (50.0%)	-	-		
	5			30.2	26.8	23.7827×10^{-2}	-0.62177
	30			32.4	22.6	15.7641×10^{-2}	-0.80245
	60			34.0	22.0	14.2352×10^{-2}	-0.84680
	90			35.0	21.0	12.6000×10^{-2}	-0.89963
3	0	204 (49.04%)	212 (50.96%)	-	-		
	5			29.0	21.0	15.2068×10^{-2}	-0.81816
	30			30.6	20.7	14.2068×10^{-2}	-0.84771
	60			31.0	20.4	13.4245×10^{-2}	-0.87224
	90			31.6	20.0	12.6582×10^{-2}	-0.89793
	120			32.0	19.6	12.0050×10^{-2}	-0.92082
	150			32.6	19.0	11.0736×10^{-2}	-0.95591

TABLE 2.8 Effect of particle size range

Length of the bed of coke particles = 12 cms.
Temperature of gasification = 1100°C
Inlet gas flowrate = 297 c.c/min. at 20°C.
Inlet gas composition = 50.0% carbon dioxide
50.0% nitrogen
Weight of the bed of coke for -22+25 particle range, B.S.S. = 28.5 gms.
" " " -60+72 " = 33.0 gms.
" " " -72+100 " = 39.5 gms.

Run No.	Sample taken at(min)	Particle size range mesh, BSS	Per cent of f-gas CO_2	CO	K calculated	Log K
1	0	-22+25	-	-		
	5		26.4	32.6	40.2598×10^{-2}	-0.39522
	30		29.6	29.4	29.2013×10^{-2}	-0.53462
	60		29.2	29.0	28.8013×10^{-2}	-0.54061
	90		28.0	28.0	28.0000×10^{-2}	-0.55284
2	0	-60+72	-	-		
	5		20.0	34.0	57.8000×10^{-2}	-0.23807
	30		18.0	44.0	107.5555×10^{-2}	+0.03140
	60		17.6	44.4	112.0090×10^{-2}	+0.0492
	90		17.0	45.0	119.1176×10^{-2}	+0.07592
3	0	-72+100	-	-		
	5		22.0	39.0	69.1363×10^{-2}	-0.16033
	30		20.2	40.8	82.4079×10^{-2}	-0.08407
	60		18.4	42.6	98.6282×10^{-2}	-0.00603
	90		18.0	43.0	102.7222×10^{-2}	+0.01157
	120		17.4	44.6	114.3195×10^{-2}	+0.05806
	150		17.0	45.0	119.1176×10^{-2}	+0.07592

TABLE 2.9 Effect of using carbon dioxide only on the equilibrium

Length of the bed of coke particles = 12 cms.
Temperature of gasification = 1100°C
Inlet gas flowrate = 148.5 c.c/min.at 20°C

Weight of bed of coke particle size range -60+72 mesh B.S.S. = 33 gms.
Weight of bed of coke particle size range -72+100 mesh B.S.S. = 39.5 gms.

Run No.	Sample taken at(min)	Particle size range mesh.BSS	Per cent off-gas CO_2	CO	K calculated	Log K
1	0	-60+72	-	-		
	5		40.2	59.8	88.9562×10^{-2}	-0.05085
	30		26.2	73.8	207.8793×10^{-2}	+0.31767
	60		24.6	75.4	231.1040×10^{-2}	+0.36380
	90		23.0	77.0	257.7826×10^{-2}	+0.41120
2	0	-72+100	-	-		
	5		40.0	60.0	90.0000×10^{-2}	-0.04576
	30		26.0	74.0	210.6154×10^{-2}	+0.32342
	60		23.2	76.8	254.2344×10^{-2}	+0.40517
	90		20.6	79.4	306.0368×10^{-2}	+0.48572

2.6.3. Sample calculations. The calculation of the equilibrium ratio for an outlet gas composition of

carbon dioxide = 40%
carbon monoxide = 17%

was as follows:

$$K = \frac{(v_{CO})^2}{v_{CO_2}} = \frac{\left(\frac{17}{100}\right)^2}{\frac{40}{100}} = \frac{289}{4000} = 7.225 \times 10^{-2}$$

$$\log K = \bar{2}.85884 = -1.14116$$

Calculation of Residence Time

Residence times were calculated for the particle size range - 16 + 18 B.S.S. as this was the only sample which had provided sufficient readings in both horizontal and vertical reaction tubes.

The true density of the particles was determined by the method of B.S.1016, part 13, 1963, and was found to be 2.26 gms/c.c. The residence times for various flowrates along with the log K values both for horizontal and vertical tubes are given in Table 2.10.

TABLE 2.10 Residence time with respect to flowrate

Flowrate c.c/min.	Residence time (min.)	Calculated Log K values for Horizontal tube	Vertical tube
198.5	0.1970	-	-0.310
203	0.1927	--0.01	-
297	0.1317	-	-0.755
407	0.0961	-0.50	-
416	0.0941	-	-0.820
608	0.0643	00.72	-
1225	0.0319	-1.61	-

The calculation of residence time for flowrate, 1320 c.c/min. and the particle size range, -16+18 mesh was made as follows:-

$$\frac{1}{4V}\left(\pi D_1^2 L - \frac{4W}{\rho}\right) \quad , = \text{Residence time}$$

$$= \frac{1}{4(0.04664)}\left[(3.14)\left(\frac{0.2}{12}\right)^2 \frac{12}{2.54(12)} - \frac{4(22.8)}{2.26(2.54)^3(12)^3}\right]$$

$$= 5.36 \times 0.005529 = 0.02964 \text{ mins.}$$

2.6.4. Reaction with carbon deposited on iron

Three experimental runs were carried out in which carbon deposited on freshly reduced iron was gasified with carbon dioxide. In each case 100 gms of the haematite ore (-16+18 mesh B.S.S.)size range) was placed in the furnace tube with its axis in a vertical direction. The ore powder was kept in position by means of a stainless steel disc perforated with a number of 1.0 mm diameter holes and supported by a steel spiral. The gas flow was arranged to be downwards from the top of the reactor and a glass condenser was included in the outlet line to collect the condensed water produced during the reduction of the ore. The duration of each reduction was 10 hours with an inlet flowrate of hydrogen of 0.013 ft^3/min. at 20°C. Since it was difficult to estimate the end of water evolution, the extent of reduction of the iron ore was tested from time to time by passing a little methane through the bed and analysing the off-gas for carbon monoxide. The non-appearance of carbon monoxide was taken as an indication of the completion of reduction of the ore to metallic iron. As soon as the reduction was seen to be complete, hydrogen flow was stopped and methane was introduced into the reactor at a rate of 0.017 ft^3/min at 20°C. After a fixed time of carbon deposition (two hours in each case), a measured flow of carbon dioxide and of nitrogen were introduced into the reactor.

The outlet gases were analysed every twenty minutes with the help of an Orsat apparatus[87] connected to the outlet line by a T-piece.

TABLE 2.11 Gasification of carbon deposited on iron

Length of the bed of iron powder = 17.4 cms.
Weight " " " = 100.0 gms.
Particle size range = -16+18 mesh B.S.S.
Inlet flowrate at 20°C of hydrogen = 0.013 ft^3/min.
" " " methane = 0.017 ft^3/min.
" " " carbon dioxide and nitrogen mixture = 0.026 ft^3/min.
Inlet gas composition = 54% carbon dioxide
= 46% nitrogen
Temperature of reduction and carbon deposition = 800°C
" " gasification = 800°C and 850°C

Run No.	Temp. C	Sample taken at(min)	Per cent off-gas CO_2	CO	K calculated	Log K
		0	-	-		
1	800	20	22.8	38.2	0.64	-0.19382
		40	26.0	32.0	0.394	-0.40450
		60	29.8	28.2	0.267	-0.57349
		80	31.4	26.6	0.226	-0.64589
		0	-	-		
2	800	20	12.6	47.4	1.780	+0.25042
		40	17.8	42.2	1.00	+0.0000
		60	24.0	37.0	0.571	-0.24336
		80	24.6	35.4	0.508	-0.29414
		0	-	-		
3	850	20	2.2	63.0	18.0400	+1.25622
		40	2.2	62.8	17.9230	+1.25334
		60	3.0	59.0	11.6033	+1.06646
		80	3.5	56.4	9.0880	+0.95847

TABLE 2.12 The values of log K for different temperatures were taken by linear extrapolation to zero time and shown in the table below, along with the theoretical value of log K.

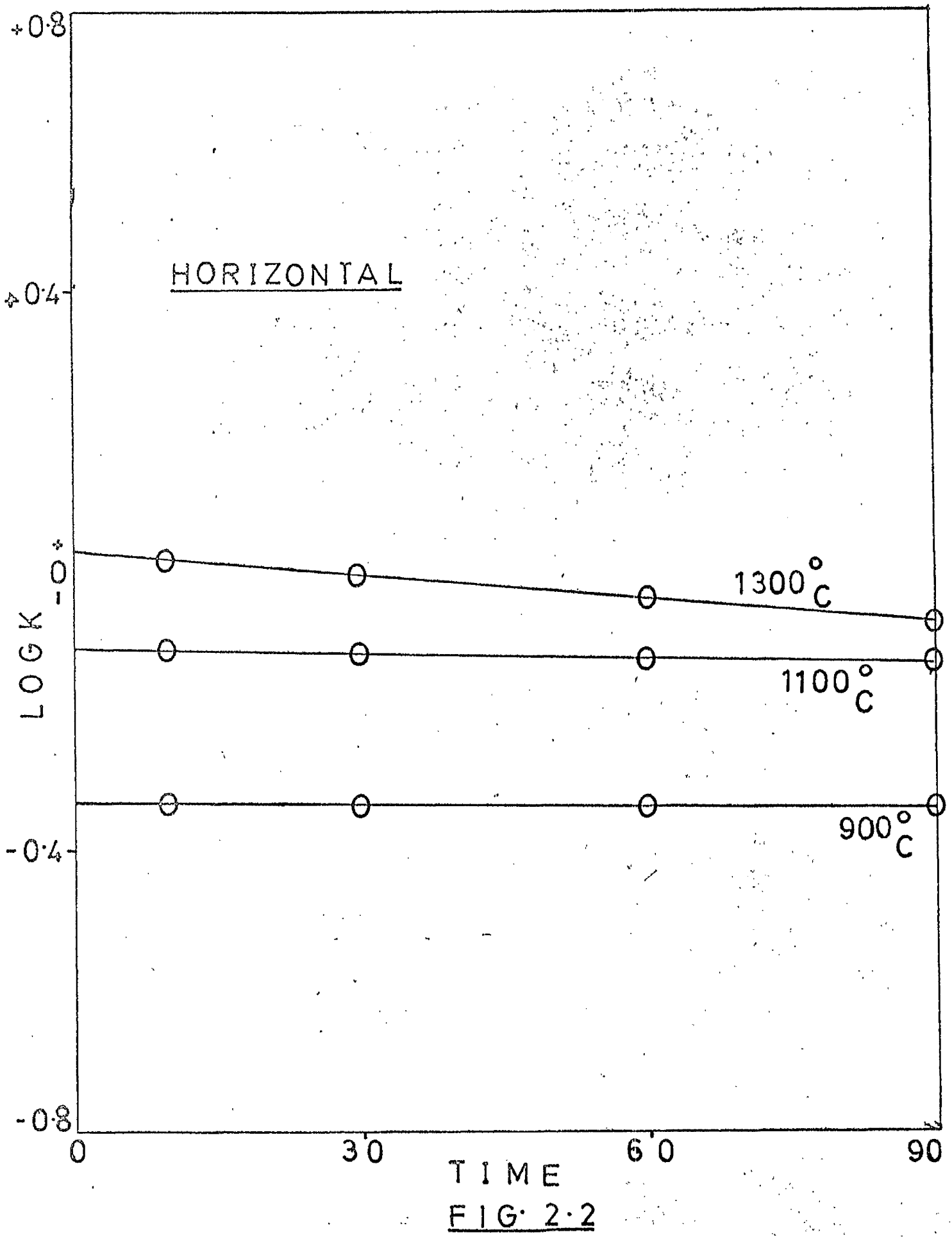
Temp. °C	Log K	
	Experimental	Theoretical
800	- 0.06	+ 0.823
800	+ 0.32	
850	+ 1.30	+ 1.20

2.6.5. Graphical presentation of the experimental results. The experimental and calculated results tabulated earlier are presented in graphic form in this section. In Fig. 2.2 is shown a plot of log K vs time for different temperatures for a horizontal reaction tube and the difference between the experimental and theoretical log K is shown in Figure 2.3.

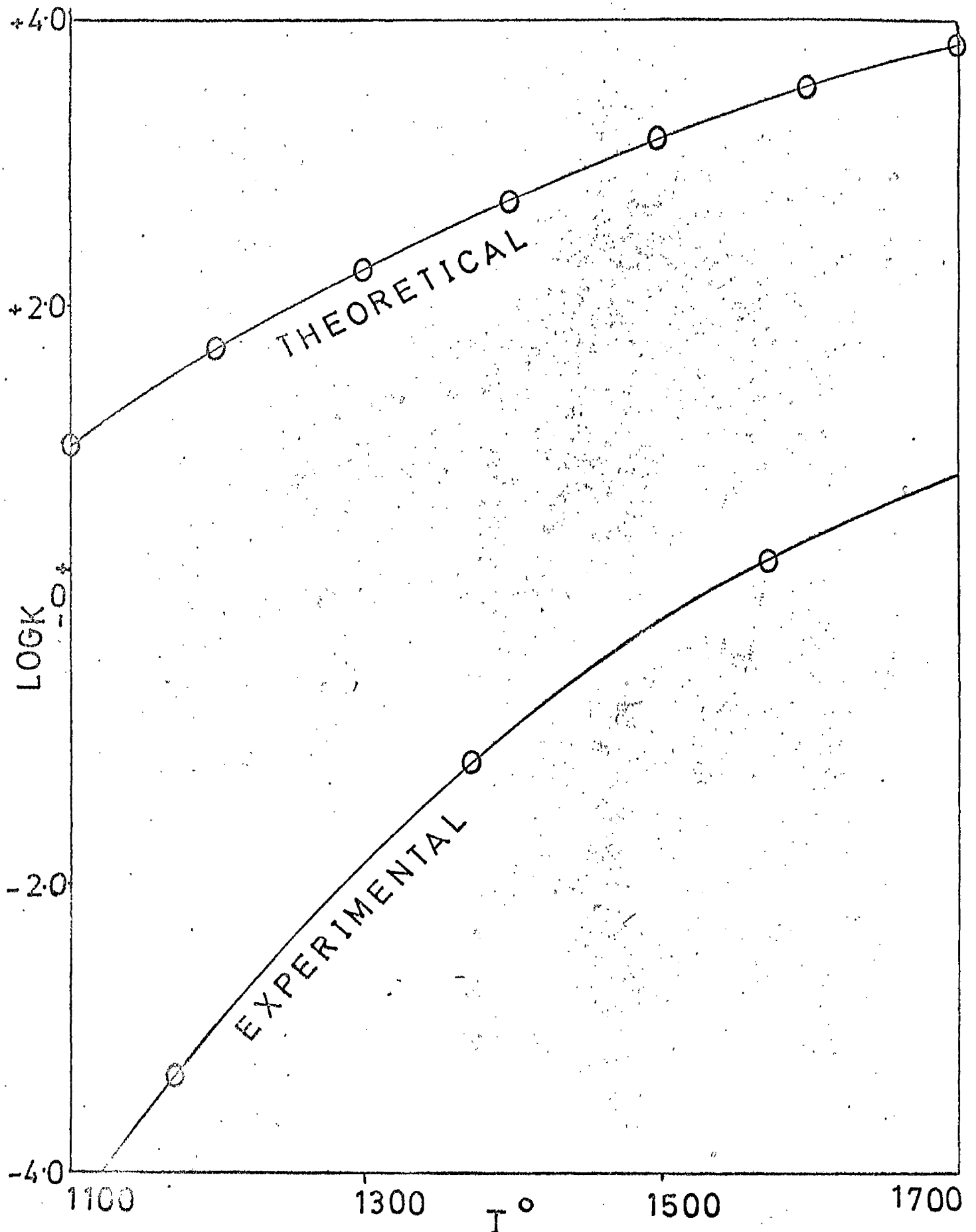
The final experimental log K values in this section, for a particular experiment were obtained by extrapolating the log K vs time line linearly to zero time.

Other log K vs time plots are shown in Figures 2.4, 2.6, 2.8 and 2.9 for different flowrates and different particle size range for both horizontal and vertical reaction tubes and difference between the ultimate log K for these experiments and the corresponding theoretical log K is shown in Figures 2.5 and 2.7 respectively. The effect of residence time of the reacting gas on the equilibrium ratios is shown in Figure 2.10.

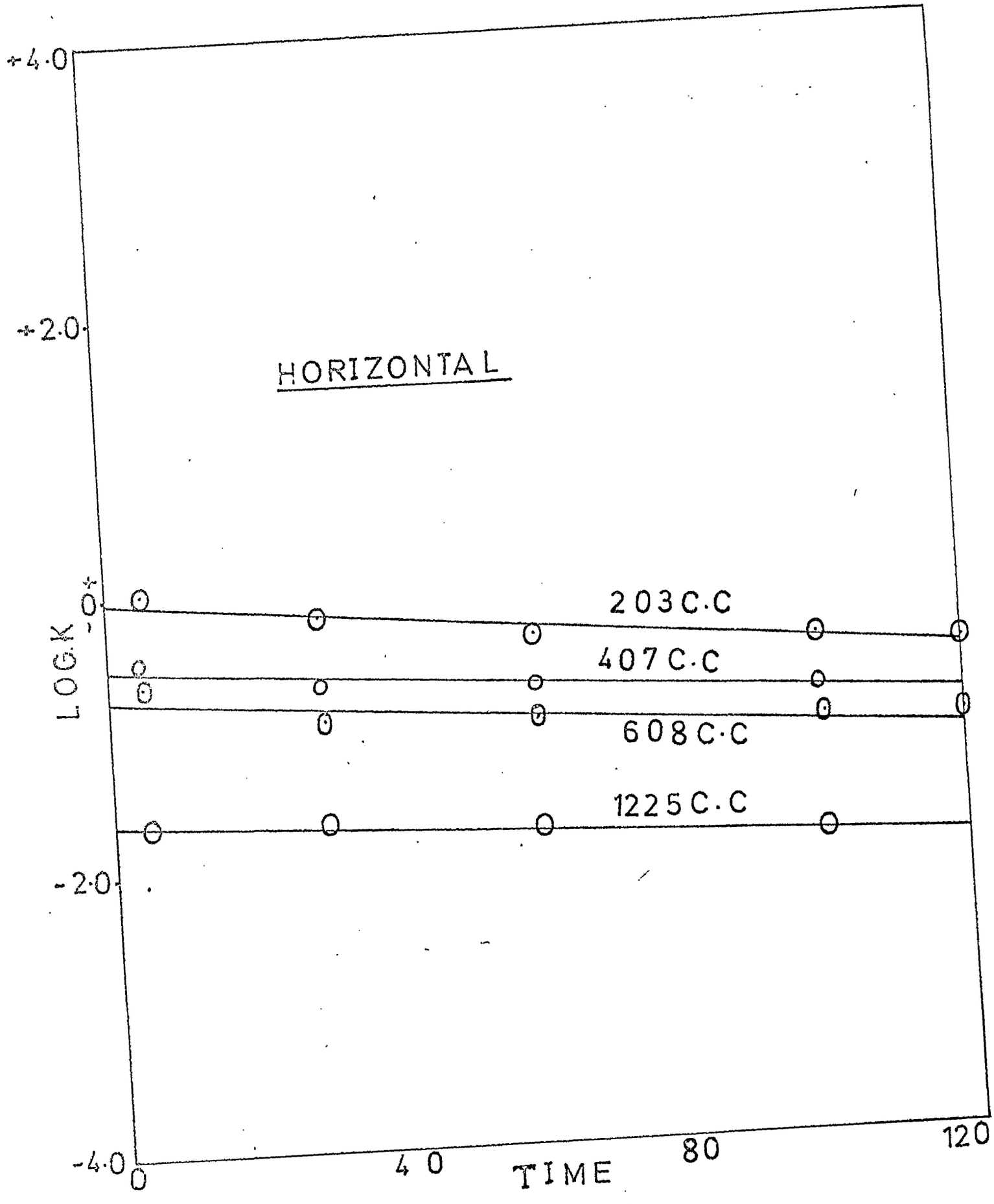
The log K vs time plots for experiments done on reduced iron with deposited carbon are shown in Figure 2.11 and the ultimate log K values for these experiments and the difference between them and theoretical values are shown in Table 2.12.



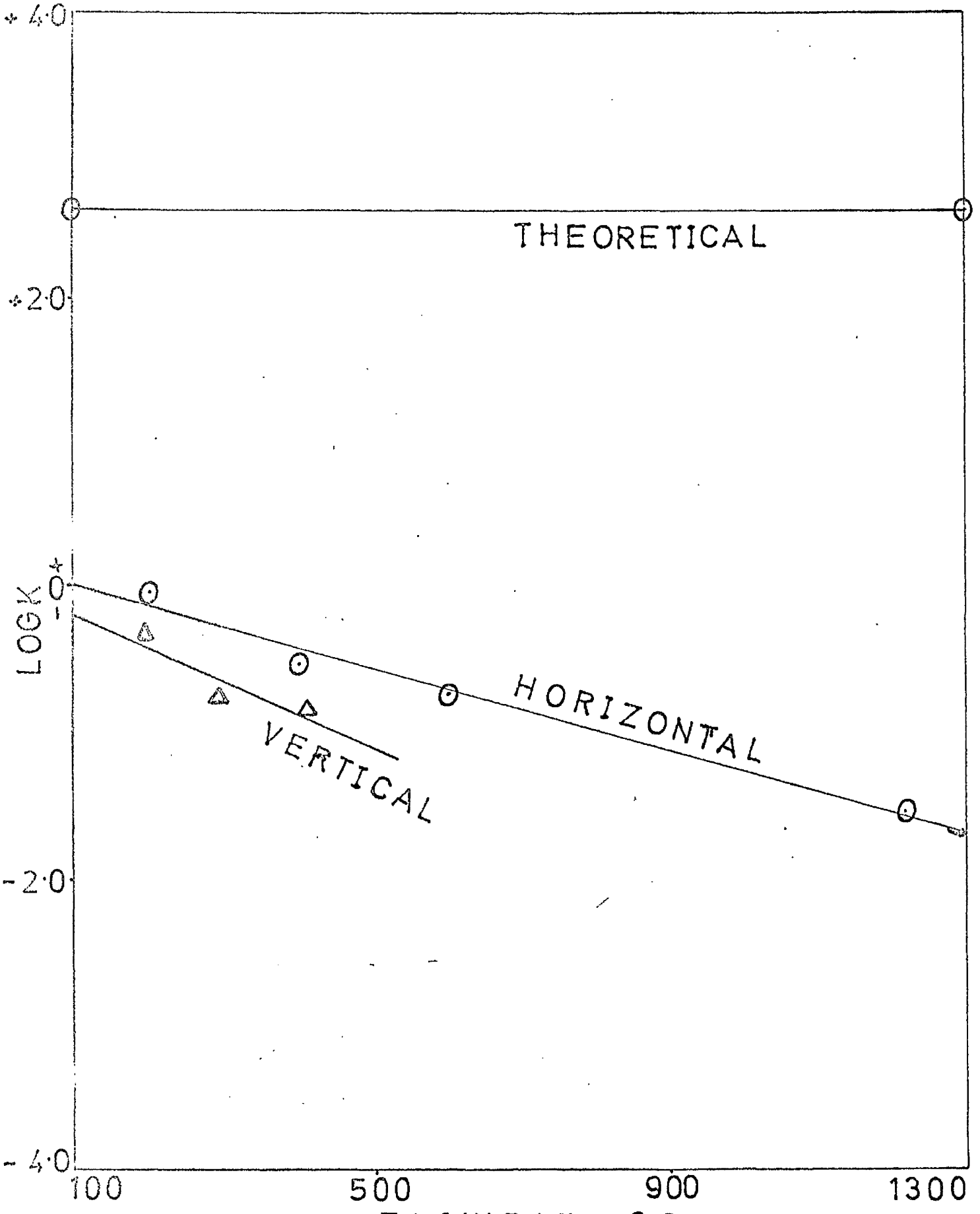
FIG· 2·2


+4·0
+2·0
-0·0
-2·0
-4·0
LOGK
THEORETICAL
EXPERIMENTAL
1100
1300
1500
1700
T °K

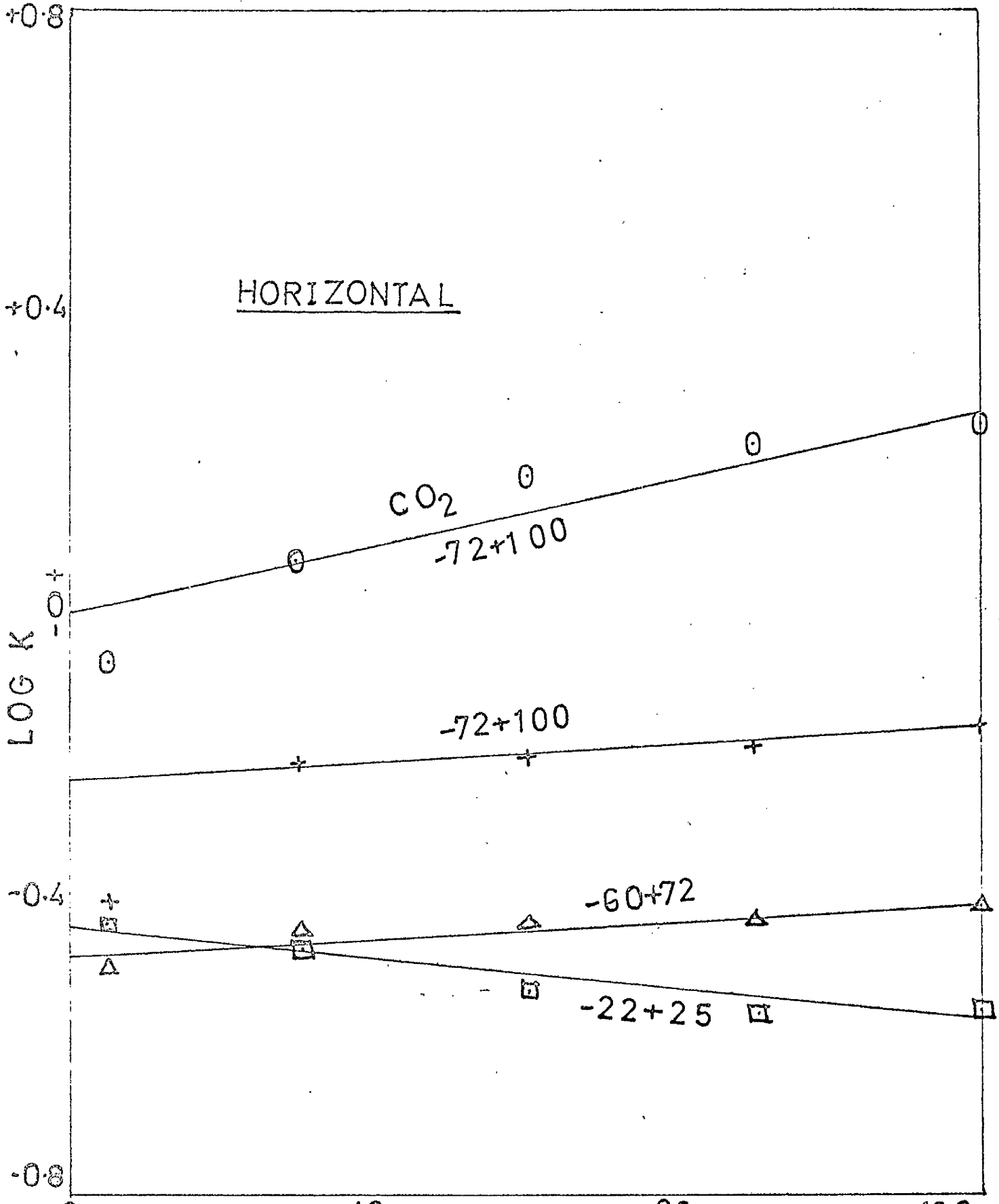
FIG·2·3


+4·0
+2·0
HORIZONTAL
LOG K*
0·
203 C·C
407 C·C
608 C·C
1225 C·C
-2·0
-4·0
0
40
80
120
TIME

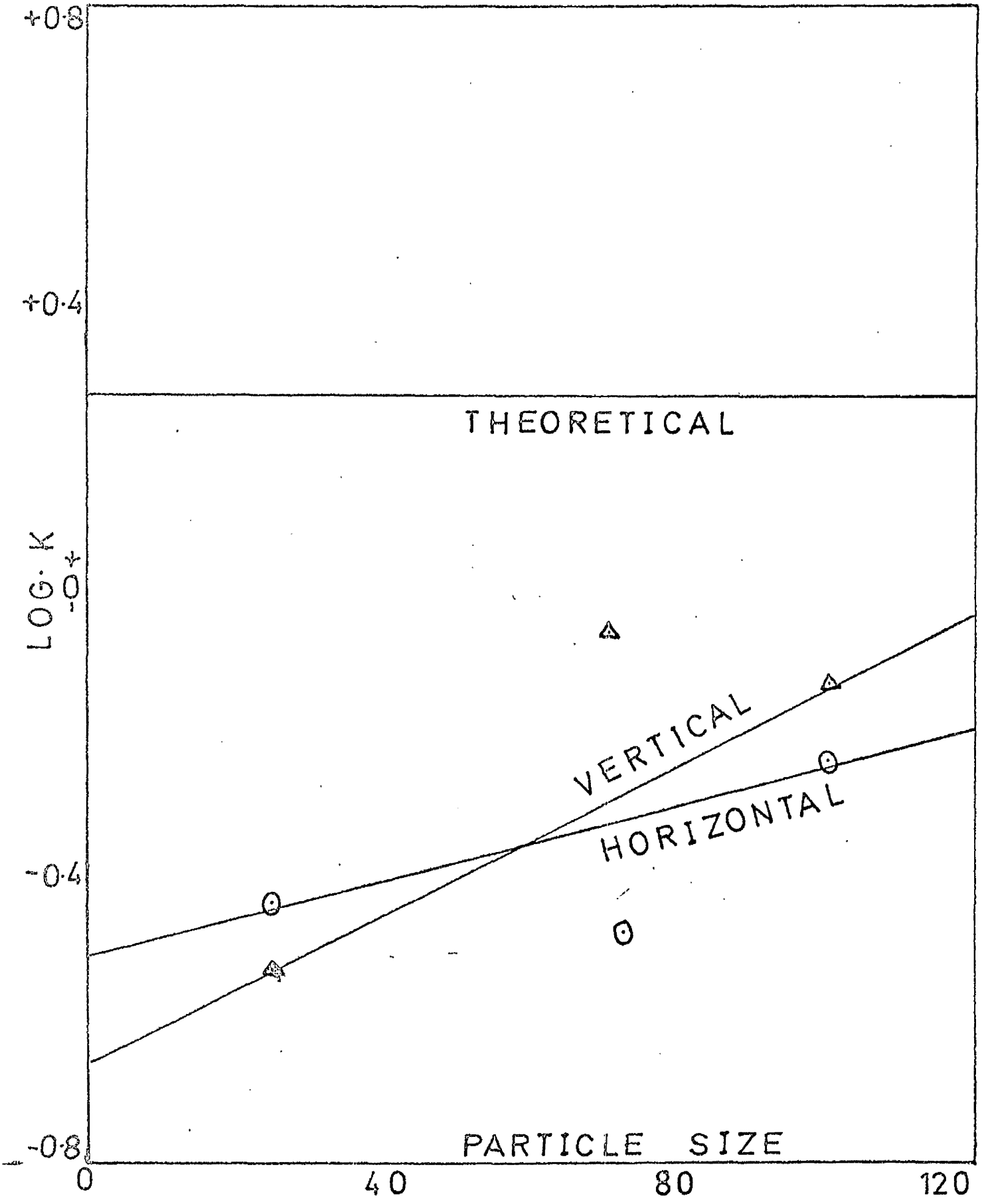
FIG·2·4


+4·0
+2·0
0
-2·0
-4·0
LOG K
THEORETICAL
HORIZONTAL
VERTICAL
100
500
900
1300
FLOW RATE, c·c/min.

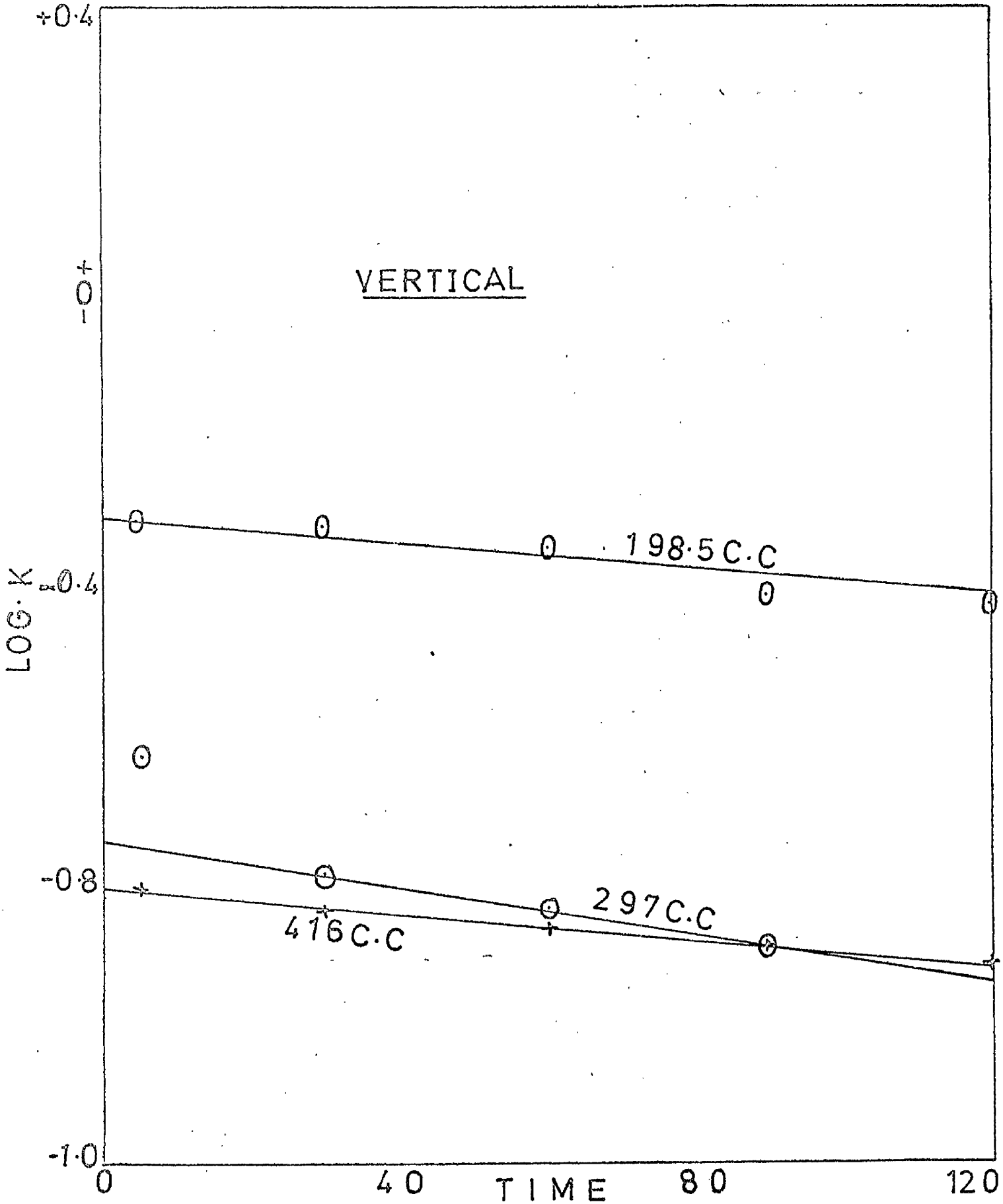
FIG·2·5


+0·8
+0·4
HORIZONTAL
CO2
-72+100
-72+100
-60+72
-22+25
LOG K
-0·4
-0·8
0
40
80
120
TIME

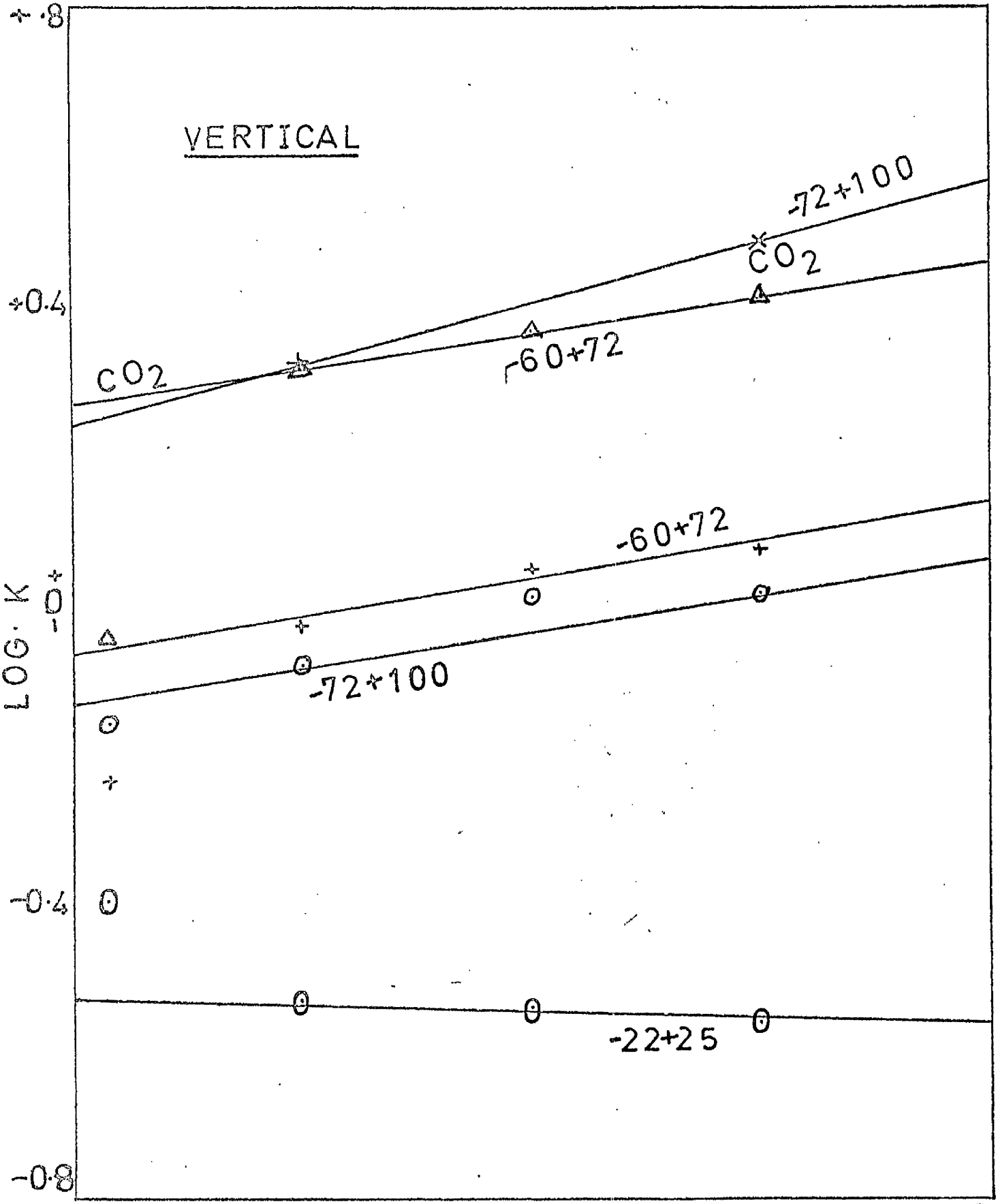
FIG·2·6


+0·8
+0·4
THEORETICAL
LOG·K
-0·
VERTICAL
HORIZONTAL
-0·4
-0·8
PARTICLE SIZE
0
40
80
120

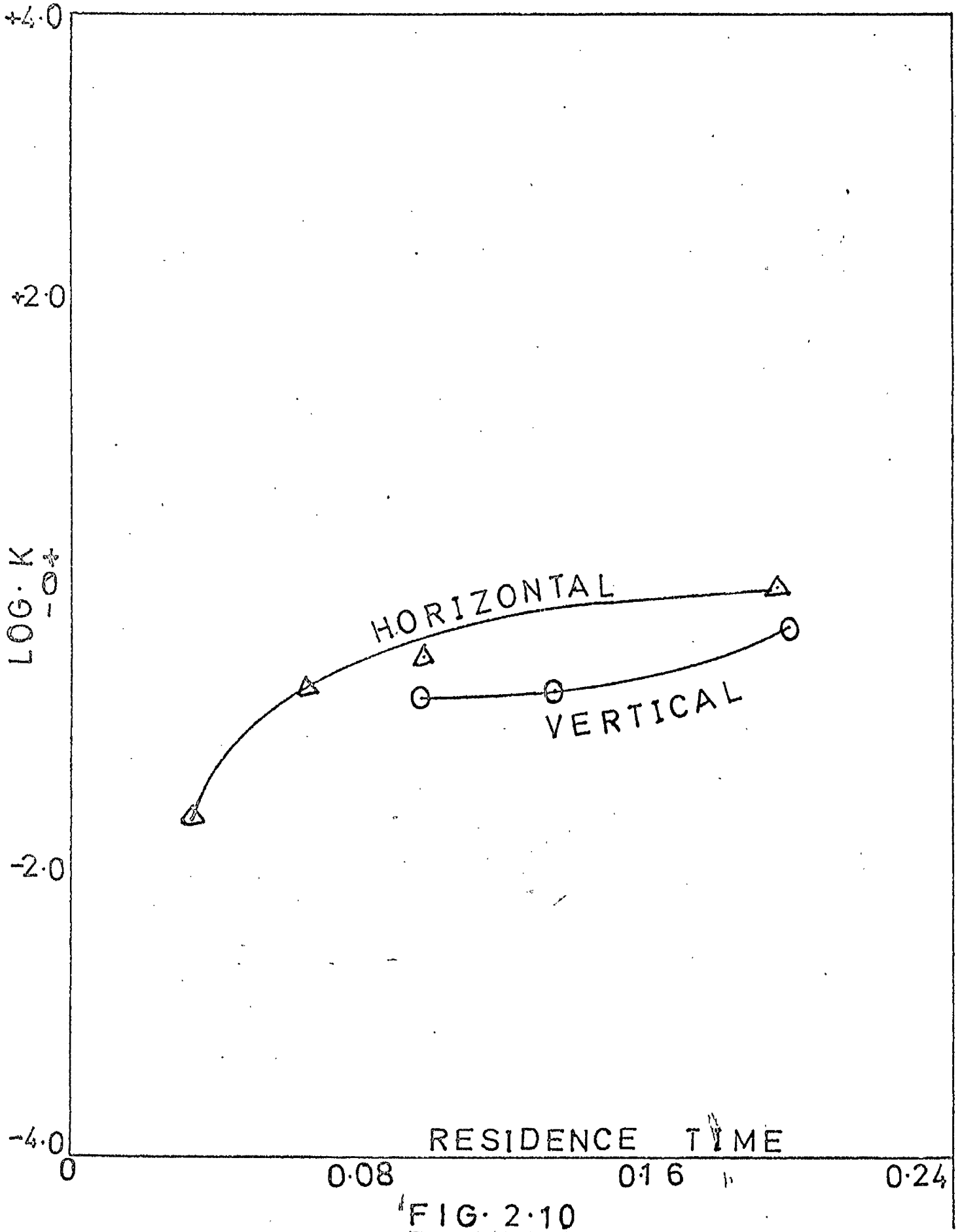
FIG·2·7



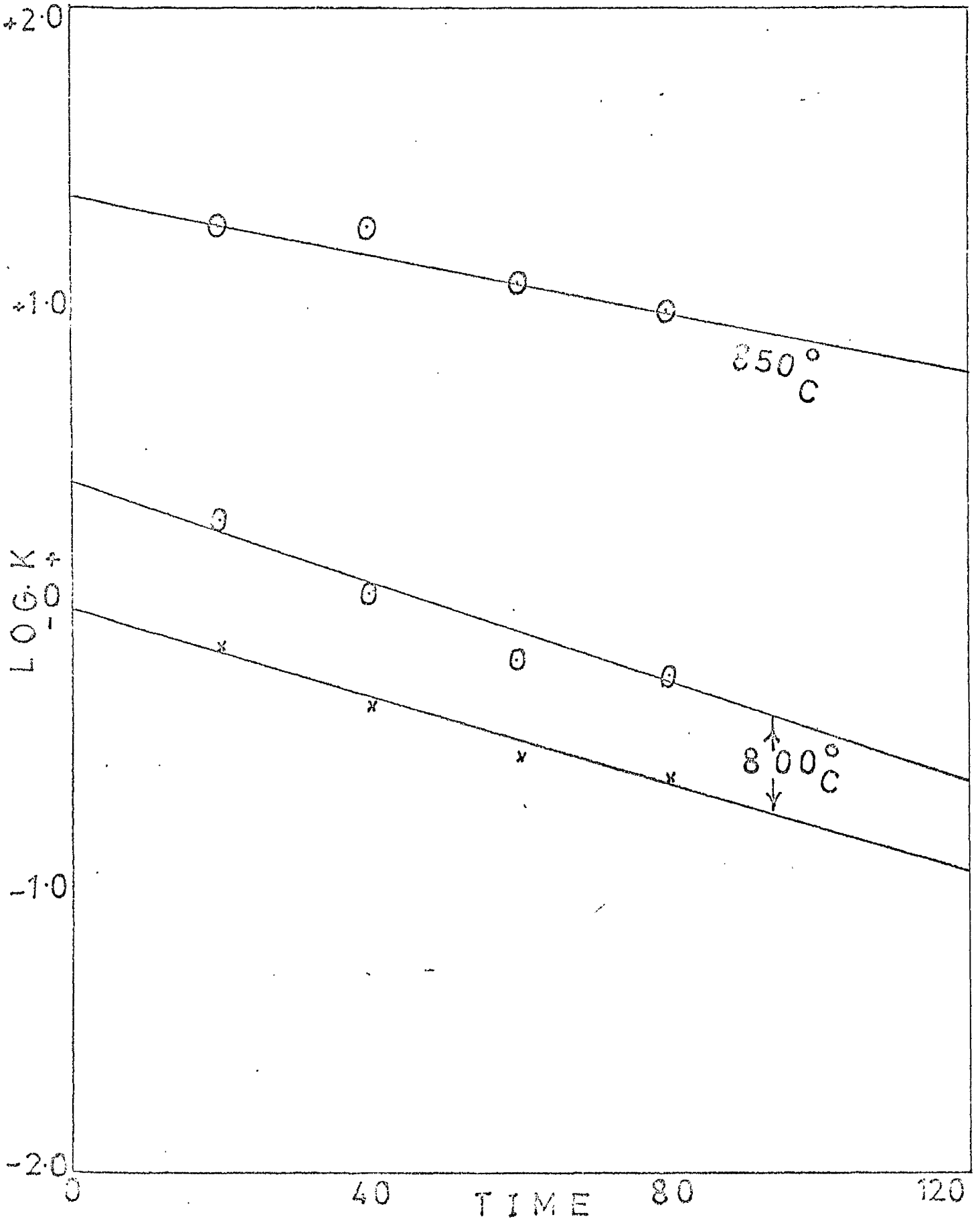
FIG·2·8


VERTICAL
+·8
+0·4
0
-0·4
-0·8
LOG·K
0
40
80
120
TIME
CO2
-72+100
CO2
-60+72
-60+72
-72+100
-22+25

FIG·2·9


+4·0
+2·0
LOG·K
-0+
-2·0
-4·0
HORIZONTAL
VERTICAL
RESIDENCE TIME
0
0·08
0·16
0·24

FIG· 2·10



FIG·2·11

2.7 Discussion of the results.

In a flow method of operation like the one described on previous pages, a representative equilibrium ratio cannot be taken by averaging the ratios obtained at different times in an experimental run. Although theoretically the amount of carbon available for reaction should have no effect on the equilibrium, and does not in fact enter into the calculation of an equilibrium constant, the progressive burn-off of carbon opens channels in the bed through which gas can by-pass and exposure of ash constituents may have a blanketing effect on the surface reaction between carbon and carbon dioxide. It can be seen from the results that in most cases the equilibrium ratio decreases with time of contact. However, in some experiments particularly with smaller carbon particles, the equilibrium ratio increased with time of contact. This might be due to slower rate of carbon burn-off. Moreover, with increase in time increasing amount of carbon surface may be coming into contact with the reacting gas. As is generally known, the smaller the particle sizes the bigger the surface they present. It is possible that a longer experimental time would have shown a decreasing tendency after a sufficient fraction of carbon had been burnt-off.

Owing to the tendency of the equilibrium ratios to decrease with time, an appropriate equilibrium ratio was obtained by extrapolating the log K vs time plot to zero time. It may be seen that in some cases the plotted lines approach the equilibrium ratio axis linearly and a zero time value is easily obtained. In other cases, however, the first sample drawn appears to give a result not in a straight line with later points. It is difficult to know in these cases whether these first points should be included in the extrapolation or excluded. In Figures 2.6, 2.8 and 2.9 in particular, the results for -72+100 mesh size range, 297 c.c/min flowrate and -22+25 and -60+72 mesh size ranges respectively appear to be out of line.

It was found that the coke carbon had little reaction to carbon dioxide at 700°C and very low reaction at 900°C. The equilibrium ratios for other temperatures were very low compared with the theoretical ones (Figure 2.3).

Three experiments were carried out using 100% carbon dioxide (Figures 2.6 and 2.9) and the equilibrium ratios were found to be higher than those obtained in experiments carried out with the same amount of carbon dioxide but diluted with an equal amount of nitrogen (Table 2.5 run No.3, and Table 2.8 run Nos. 2 and 3). Perhaps the equilibrium ratios would not have been so high, had it been possible to use the same flowrate in all cases. As it was shown in other experiments (Figures 2.4 and 2.8) that increase in

flowrates decreased the equilibrium ratio by decreasing the residence time of the reacting gas in the reactor, the same argument could well be applied to the case of 100% CO_2 flow where the residence time was double that of the mixture.

The extent of the reaction was also influenced by the increase in particle sizes used. Higher equilibrium ratios were obtained with the smaller particle size ranges than with the larger ones, with the same flowrate of gas and at the same temperature. The smaller particles offer a larger amount of reaction surface per unit volume and also cause higher gas velocities between the particles than do the larger particles. Two anomalies, however, were observed with the -22+25 mesh particles in horizontal reaction tube, and the -60+72 mesh particles in the vertical reaction tube. In both cases, the equilibrium ratios obtained were higher than those obtained with smaller particles such as -60+72 mesh in the second case. No explanation could be offered for these anomalies as the conditions of reaction were the same in all cases.

The percentage of carbon removal with time from the bed was also calculated for several runs for both horizontal and vertical positions. It may be seen from Figure 2.12 that the percentage removal of carbon from the bed has a linear relationship to duration of run.

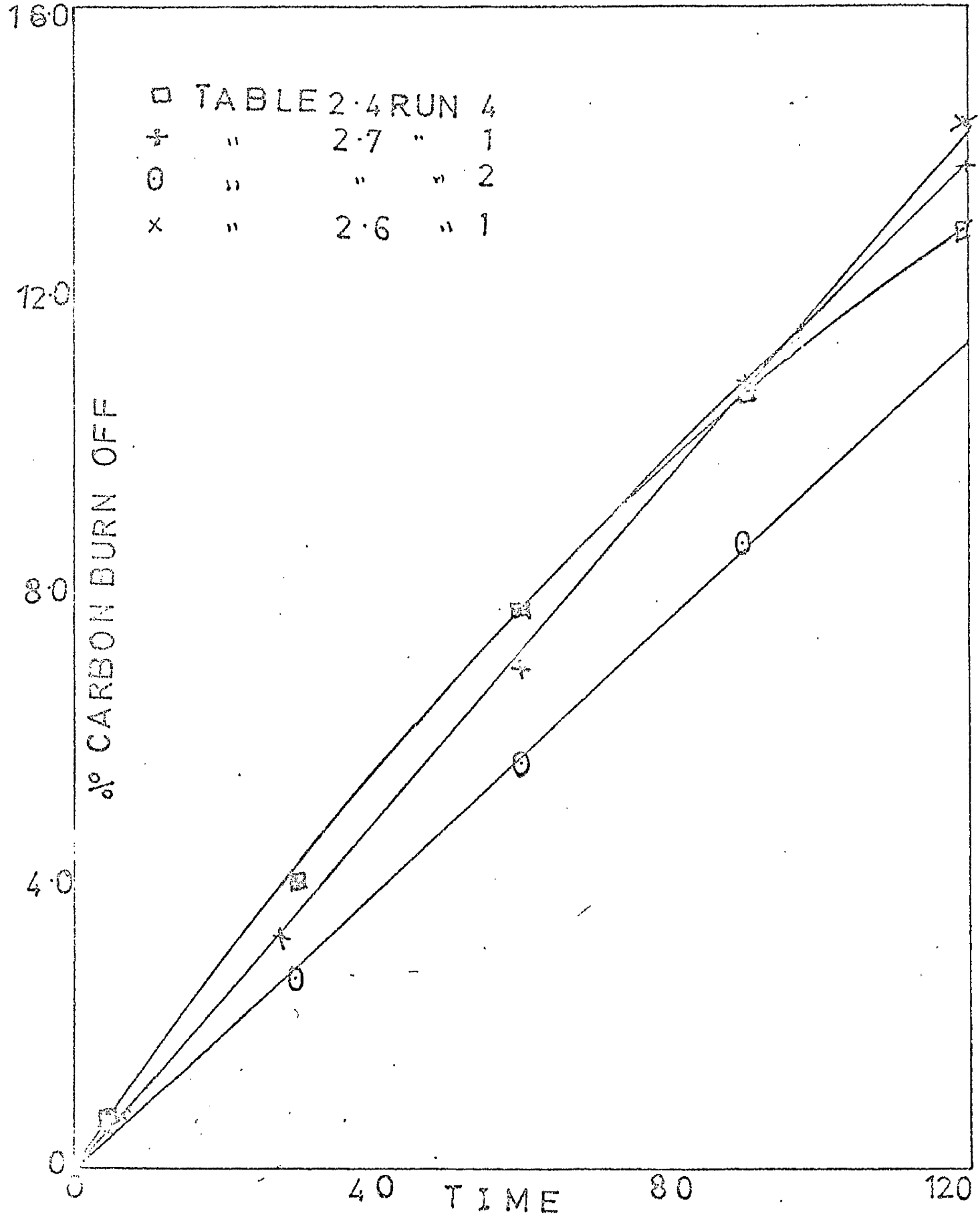


TABLE 2·4 RUN 4
" 2·7 " 1
" " " 2
" 2·6 " 1
% CARBON BURN OFF
TIME
0
4·0
8·0
12·0
16·0
40
80
120

FIG-2·12

The percentage carbon removal was calculated by a nitrogen balance for three cases (Run No.4 of Table 2.4), Run No.1 and 2 of Table 2.7). For Run No.1 of Table 2.6 where no nitrogen was used, the calculation was carried out by correlating the percentages of carbon monoxide and carbon dioxide of the exit gases with the inlet flowrate. A typical nitrogen balance calculation is shown below, e.g. for Run No. 4 of Table 2.4.

Flowrate of nitrogen = 101.5 c.c/min at 20°C.

Exit gas percentages = 18.4% carbon dioxide, and 43.6% carbon monoxide.

Inlet gas composition = 50% nitrogen, and 50% carbon dioxide.

Calculation

Moles of carbon dioxide entering the reactor per hundred moles of nitrogen $= \frac{50(100)}{50} = 100$

∴ gm. atoms of carbon entering per hundred moles of nitrogen = 100

Total amount of carbon dioxide and carbon monoxide in the exit gas = 62%

Nitrogen in the exit gas = 38%

∴ gm. atoms of carbon in the exit gas per hundred moles of nitrogen $= \frac{62(100)}{38} = 163$

Excess gm. atoms of carbon going out per hundred moles of nitrogen = 163-100 = 63

or 0.63 gm. atoms of carbon per mole of nitrogen.

Weight of coke in the bed = 22.8 gms.

Ash content of the coke = 11.2%

Therefore if we make the assumption that coke contains only "carbon" and "ash", total gm. atoms of carbon in the bed $= \frac{(22.8)(0.888)}{12}$

$\therefore$ gm. atoms of carbon gasified per minute $= \frac{(0.63)\ 101.5\ (273)}{(1000)\ 293\ \ (22.4)}$

$\therefore$ percentage "burn-off" per minute

$$= \frac{(101.5)273(0.63)12(100)}{(1000)293(22.4)22.8(0.888)}$$

$$= 0.157\%$$

$\therefore$ For five minutes $= 0.157 \times 5 = 0.785\%$

The rate of carbon gasification may be calculated alternatively by a carbon balance and the stoichiometry of the equation

$$C + CO_2 = 2\ CO.$$

It was found that the results obtained by such a calculation checked well with those of the nitrogen balance as calculated above.

The experiments that were carried out with the reduced iron and deposited carbon in the fixed bed were beset with difficulties, due to the carbon partially blocking available passages through iron-packed bed. This caused a significant back-pressure to develop thus causing leaks and putting the results given by the flowmeter into error. However, the analysis of the off-gas showed the sought for augmented reaction on iron. Theoretical equilibrium had been approached at 800°C and seemed to be surpassed at 850°C (Figure 2.11 and Table 2.12).

It has been stated in the introduction that both Van Wormer[36] and Gibb[29] found that the Boudouard equilibrium could be exceeded when the reaction was carried out over reduced iron in a fluidized bed. An indication in support of this prediction has been obtained for a fixed-bed (850°C).

It appeared worthwhile to continue these experiments in a fluidized bed where reaction conditions could be better controlled and results would be more reproducible.

3. FLUID-BED STUDIES IN A MILD STEEL BENCH-SCALE REACTOR.

The preliminary fixed-bed studies had shown that in spite of the large excess of carbon in the bed, steady-state reaction conditions could not be obtained. The extent of reaction decreased with time even after only a small amount of the coke had been gasified. It was therefore impossible to decide which value of equilibrium ratio one should accept as being unique for any given set of reaction conditions.

Moreover, due to the inevitable temperature gradients associated with a fixed-bed, the exact reaction temperature was not known. Even if it had been possible to introduce a thermocouple into the coke bed, a variation in temperature would have been obtained between the ends and the middle of the bed. For these reasons all later studies were made on fluidized beds of particles.

3.1. The development of fluidization and its utility.

The fluidized-bed technique is one of the most interesting chemical engineering developments of the past twenty-five years. With the lapse of time, it has proved to be an extraordinary versatile tool to the chemical engineering profession. From its start in the late thirties and forties, this technique has had wide application in the

petroleum and chemical process industries. Though first utilized in the Winkler gas generator in Germany in the late twenties[88], the modern concept was actually developed in the chemical engineering laboratory of the Massachusetts Institute of Technology by Professors W.K. Lewis and E.R. Gilliland. Their basic studies of the flow properties of solids suspended in gases, coupled with the ingenious concept of the stand-pipe for catalyst feed to a fluidized bed resulted within two years in the completion of a full-scale commercial plant for the catalytic cracking of petroleum feed-stock.[89]

The inherent qualities of a fluidized-bed are :-

(a) a high degree of mixing and intimate contact between solid and gases,

(b) uniform distribution of the solids throughout the bed,

(c) high heat transfer between gas and solids, and from point to point in the bed and between bed and the reactor walls, and

(d) easy removal and withdrawal of products.

Its main disadvantages are:-

(a) frequent erosion of the reactor vessel, and

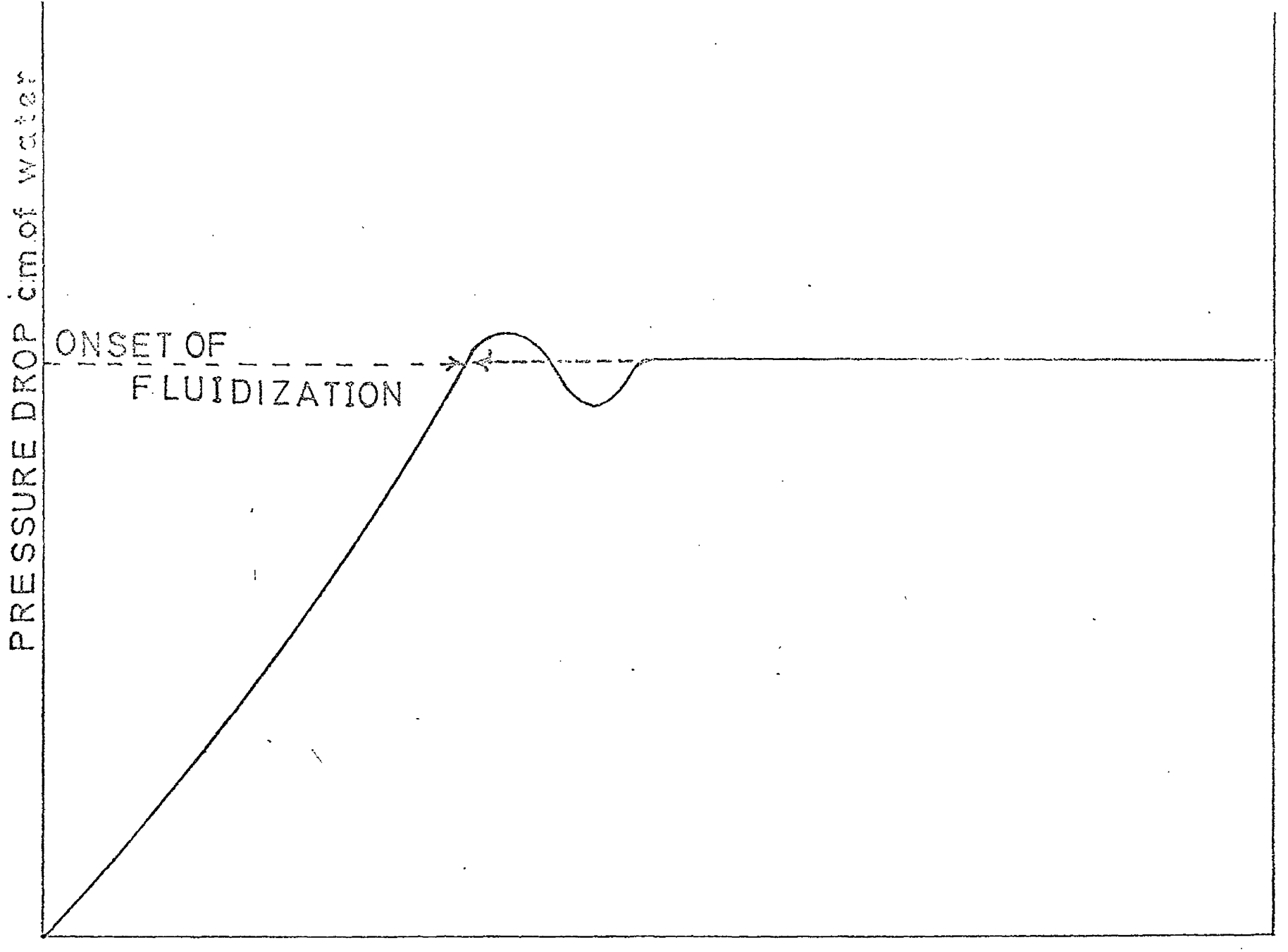
(b) carry-over of fines formed due to attrition of the particles.

It may be said, however, that for many purposes the advantages far outweigh the disadvantages.

The agitated state of the particles in a fluidized-bed helps in exposing greater surface area to the reacting gases, thus ensuring a high reaction rate. Moreover, due to the low temperature gradients throughout the bed, the temperature of the bed can be maintained within narrow known limits. This is of great value in kinetic and equilibrium studies of gas-solid reactions.

3.2. Mechanism of fluidization.

When a fluid is made to flow through a dense bed of granular solids, the fluid passes through the interstices between the particles and experiences frictional resistance. This resistance of the bed to the flow of the fluid causes a fluid pressure-drop to be developed across the bed. The pressure drop increases with the increase of fluid-flow until a maximum value is reached, when the bed offers a maximum resistance. At this point, the pressure-drop is approximately equivalent to the weight of the bed and the bed becomes airborne. With further increase of the flow, the resistance of the bed suddenly falls a little and the particles in the bed begin to move. This point is that of the onset of fluidization or minimum fluidization. With further increase of fluid flowrate, the pressure drop across the bed remains approximately constant but the bed expands and ultimately reaches a maximum expansion. The bed now is in violent motion and carry over of particles


PRESSURE DROP cm of water
ONSET OF
FLUIDIZATION
FLUID FLOWRATE, ft3/min.

FIG·3·1

is taking place. Ultimately the whole bed is entrained by the gas and passes out of the reactor. In Figure 3.1 a pressure-drop-flow diagram for a hypothetical idealised fluidization is given.[90]

3.3. Bench-scale apparatus.

This apparatus consisted of the following parts :-

(a) Reactor and gas-preheater.

(b) Furnace.

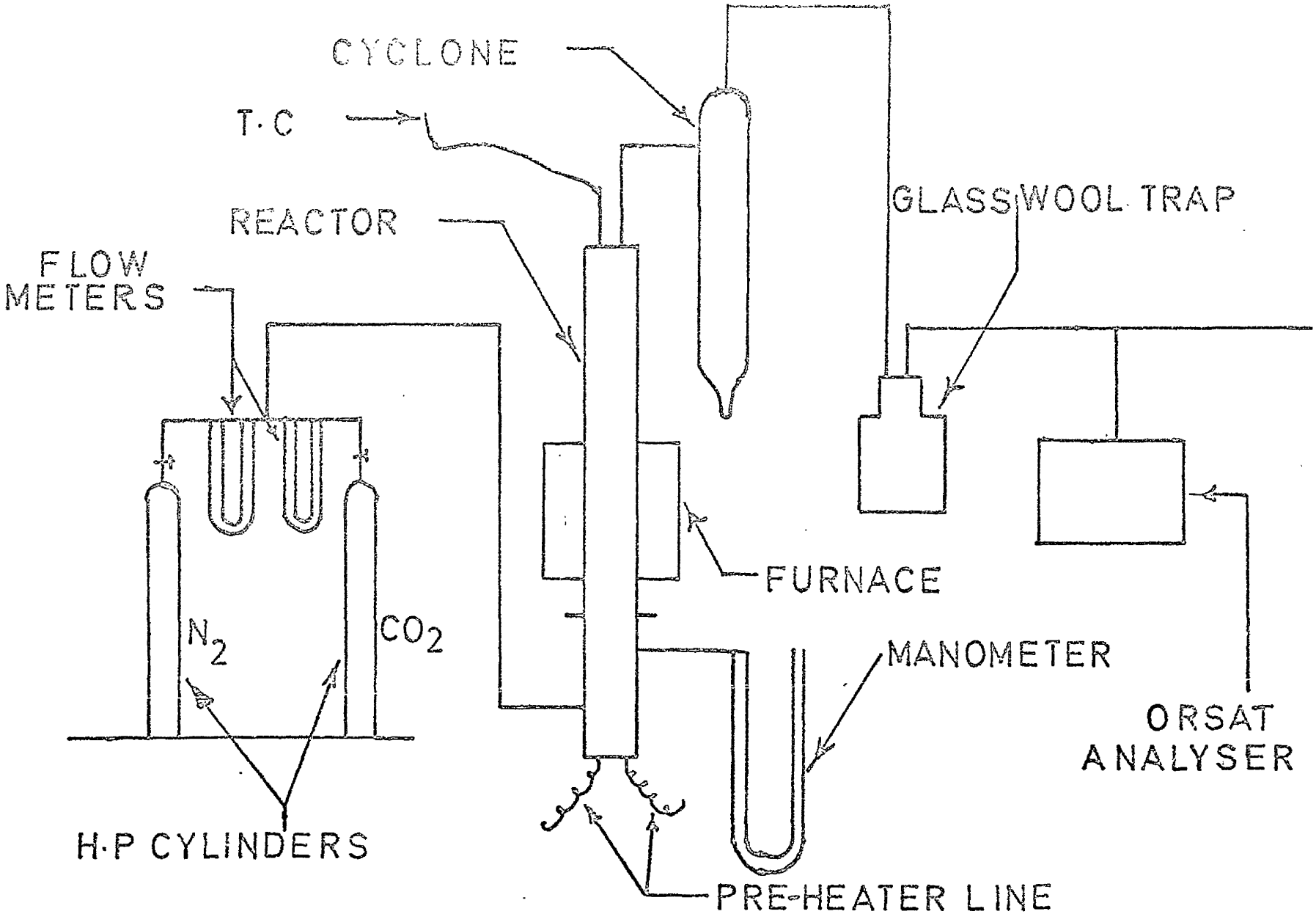
(c) Gas cleaning and metering equipment.

(d) Gas analysis apparatus.

A flow-sheet is shown in Figure 3.2.

3.3.1. Reactor. The reactor consisted of two sections of 2 inch I.D. mild steel pipe with a wall thickness of 1/8 inch, each flanged at one end and the flanges bolted together, with a stainless steel sintered disc of approximately 2.76 thousandths of an inch pore size held between them. The outer ends of the assembled pipe reactor were screwed and fitted with suitable end pieces, having gas inlet and exit points. A pressure tapping was provided just below the sintered disc to enable the total pressure drop through the whole system to be measured. The assembled reactor was supported in a vertical position on a tubular steel framework.

3.3.2. Gas-preheater. This was a heating element, with a capacity of 750 watts as normally used in a bowl-type domestic electric radiator. It was mounted inside reactor tube below the sintered disc. It had an outside diameter of



FLOW SHEET OF BENCH-SCALE FLUID-BED APPARATUS

FIG· 3·2

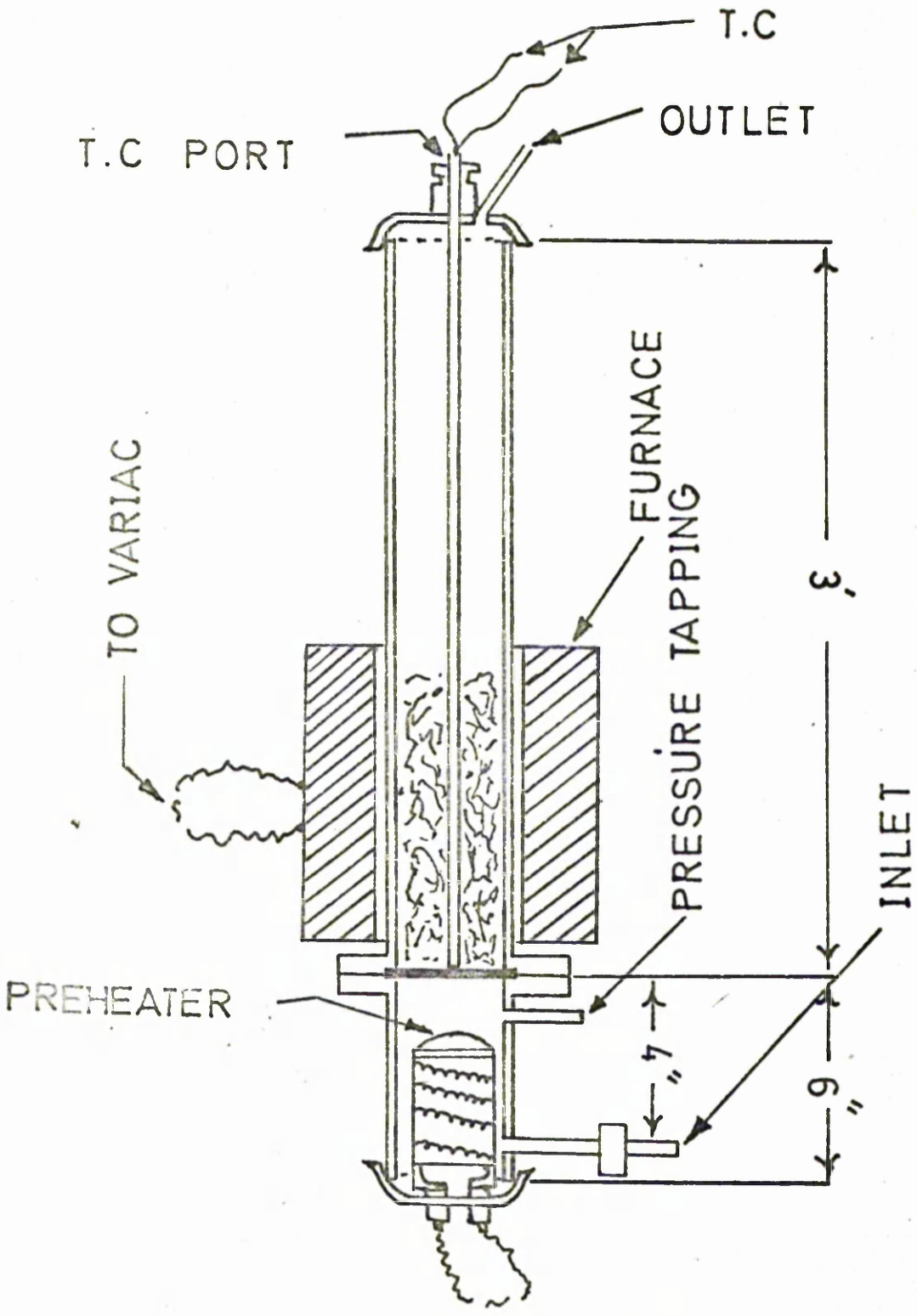
$1^5/8$ inch and thus provided a clearance of 3/16 inch all around, between the reactor wall and itself. Insulation pieces were provided to separate the element from the steel end-piece of the reactor tube. These were fabricated from Sindanyo. Electric power to the element was supplied through a "Variac" voltage regulator, with a 0 - 4 amp. ammeter in series.

3.3.3. Furnace. Heat was supplied to the reactor by a 3 Kw tubular ($2^3/4$ inch I.D.) electric furnace operating at 270 V and giving a maximum temperature of 1200°C. The furnace was controlled by a "Variac" voltage regulator and series ammeter. When fitted over the reactor, the base of the furnace rested on the flanged joint. Figure 3.3. shows an assembled view of the reactor, furnace and pre-heater.

3.3.4. Gas metering. The inlet gases, carbon dioxide and nitrogen, were metered separately by calibrated manometric flowmeters using concentrated sulphuric acid as manometric fluid.

3.3.5. Gas cleaning. The exit gases from the reactor, before analysis, were cleaned initially by a glass cyclone and then by passing through a trap packed with glass wool.

3.3.6. Gas analysis. This was a British Standard Orsat apparatus[87] which drew its sample from the gas exit line through a suitably placed T-piece. By means of this



BENCH-SCALE REACTOR SYSTEM

FIG·3·3

apparatus it was possible to determine carbon dioxide, oxygen and carbon monoxide in the exit gas. The nitrogen content was estimated by difference.

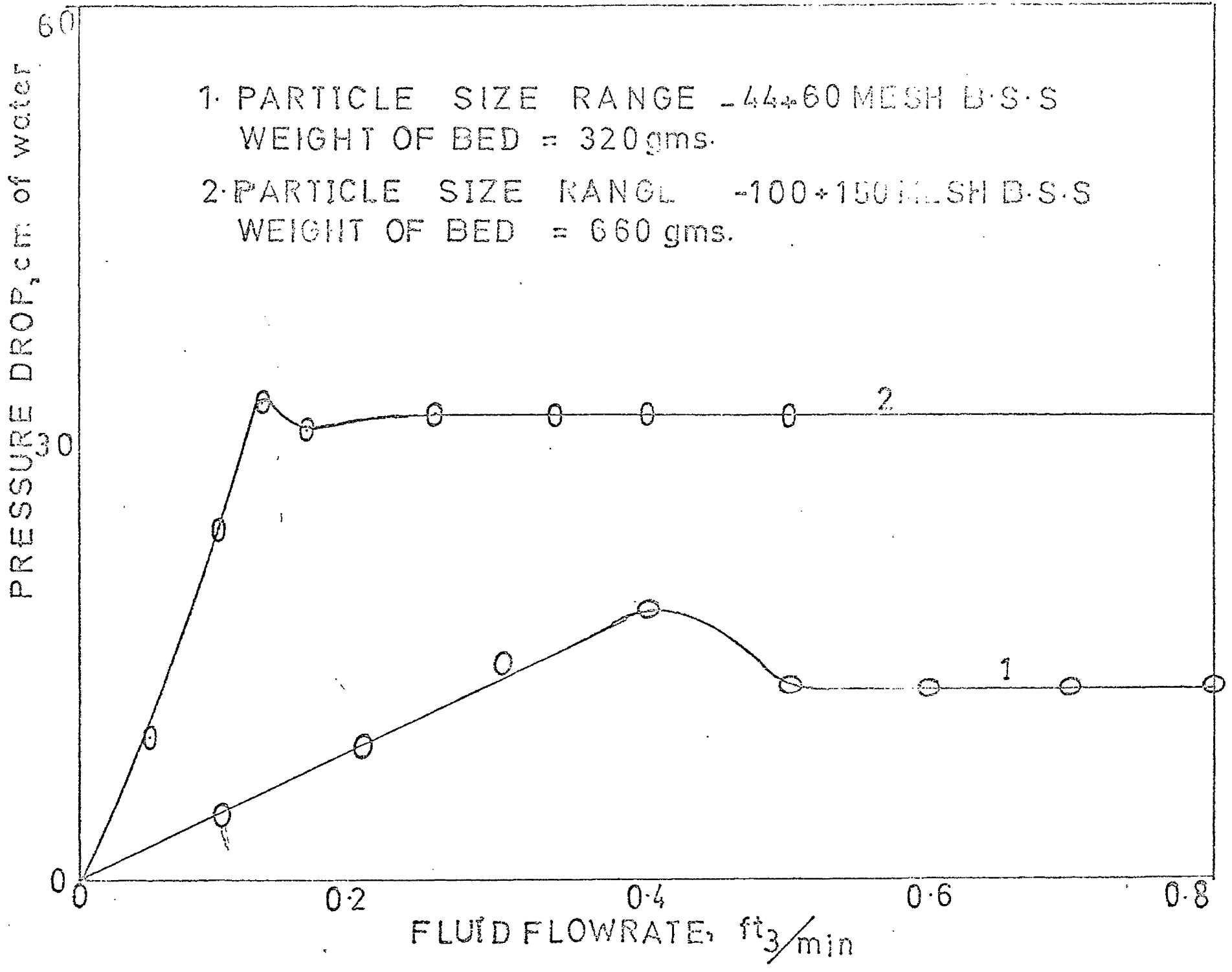
3.3.7. Temperature measurement. The temperature of the bed was measured by a travelling Chromel-Alumel thermocouple linked to a temperature calibrated millivoltmeter. The thermocouple could be moved vertically within a 1/4 inch I.D. silica pocket which was clamped through a gas-tight seal on the reactor cover passed down through the fluidized-bed and rested on the centre of the sintered stainless steel disc.

3.4. Pressure-drop-flow diagram for fluidized-bed.

As it was intended to fluidize within the reactor finely divided coke, several prior experiments were carried out to determine the fluidization performance of the powdered coke with the particular particle size range to be used. The pressure-drop-flow diagrams constructed from experimental data are shown in Figure 3.4.

3.5. Experimental procedure.

The reactor was charged with powdered coke of a particular size range for each experiment and was fluidized with nitrogen while being heated to the required reaction temperature. The flow of nitrogen was then reduced simultaneously with the introduction of carbon dioxide so


1. PARTICLE SIZE RANGE -44+60 MESH B.S.S
WEIGHT OF BED = 320 gms.
2. PARTICLE SIZE RANGE -100+150 MESH B.S.S
WEIGHT OF BED = 660 gms.
PRESSURE DROP, cm of water
60
30
0
0
0·2
0·4
0·6
0·8
FLUID FLOWRATE, ft3/min
1
2

FIG·3·4

TABLE 3.1

Coke particle size mesh	Temp. °C	Flowrate, ft^3/min. at 20°C N_2	Flowrate, ft^3/min. at 20°C CO_2	Sample taken at(min.)	Off-gas Analysis % CO_2	Average CO_2	% CO	Average CO	K calculated average	Log K
-44+60	600	0.1166	0.130	5	51.0	51.157	0.4	0.2857	1.595×10^{-5}	-4.79722
		"	"	25	51.4		0.3			
		"	"	45	51.0		0.2			
		"	"	65	51.1		0.2			
		"	"	85	51.4		0.4			
		"	"	105	51.1		0.2			
		"	"	125	51.1		0.3			
	700	0.09166	0.125	5	54.8	55.133	0.4	0.4	2.902×10^{-5}	-4.53731
		"	"	25	55.4		0.4			
		"	"	45	57.6		0.4			
		"	"	65	53.1		0.4			
		"	"	85	54.6		0.4			
		"	"	105	55.3		0.4			
	800	0.0933	0.1316	5	59.5	57.43	1.0	1.0	1.741×10^{-4}	-3.75919
		"	"	25	56.0		1.0			
		"	"	45	56.8		1.0			

TABLE 3.2

Coke particle size mesh	Temp. °C	Flowrate, ft³/min. at 20°C N_2	Flowrate, ft³/min. at 20°C CO_2	Sample taken at (min.)	Off-gas Analysis % CO_2	Average CO_2	% CO	Average CO	K calculated average	Log K
-100+150	600	0.07	0.06916	5	50.6	52.275	0.4	0.4	0.306×10^{-4}	-4.51428
		"	"	25	52.5		0.4			
		"	"	45	53.4		0.4			
		"	"	65	52.6		0.4			
	700	0.07	0.06833	5	48.8	49.3	0.6	0.52	0.3484×10^{-4}	-4.26090
		"	"	25	48.0		0.4			
		"	"	45	51.2		0.6			
		"	"	65	47.4		0.5			
		"	"	85	51.1		0.5			
	800	0.07	0.06833	5	47.8	49.0	1.3	1.3	0.345×10^{-3}	-3.46218
		"	"	25	50.2		1.3			
	900	0.0633	0.0775	5	34.7	35.95	17.1	16.775	0.7827×10^{-1}	-1.10640
		"	"	25	36.1		16.9			
		"	"	45	36.9		16.7			
		"	"	65	36.1		16.4			
	1000	0.0866	0.0758	5	19.2	19.1	41.6	42.05	0.924	-0.03433
		"	"	25	19.0		42.5			

that the total inlet gas flowrate was maintained constant. Within five minutes from the start of introducing carbon dioxide the first exit gas sample was collected. Further samples were collected at 20 minute intervals for the remainder of the reaction period.

In all, eight experiments were carried out using two size ranges of the coke. The relevant data for the coke were as follows :-

-44+60 mesh B.S.S.:

weight taken = 320 gms.

unexpanded bed depth = 9 inches

-100+150 mesh B.S.S.:

weight taken = 660 gms.

unexpanded bed depth = 16.6 inches

The results obtained are set out in Tables 3.1 and 3.2.

3.6. Discussion of the results.

In the experiments described on the previous pages, only two types of particle size ranges were used. These were -44+60 and -100+150 mesh B.S.S. The majority of the experiments were carried out with the -100+150 mesh particle size range because it was found to have better fluidization characteristics at the flowrates used.

In all, eight experiments were carried out. The -44+60 mesh material was tested at three different

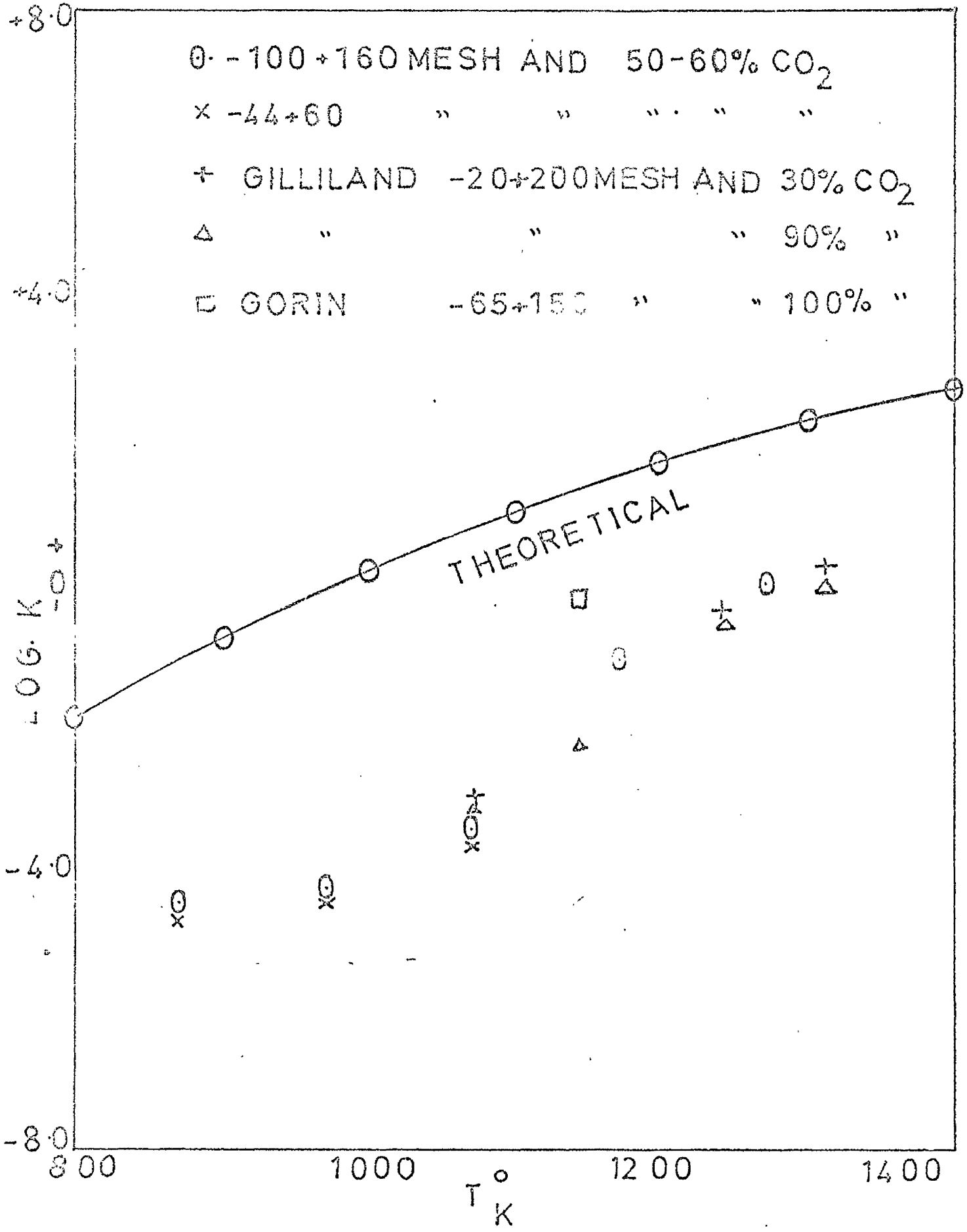
temperatures and the -100+150 mesh at five different temperatures. The extent of reaction at 600°C, 700°C, and 800°C was found to be almost identical for both particle size ranges, minor differences in the equilibrium ratios obtained were perhaps due to the different flowrates necessary for adequate fluidization.

Quantitative comparison of these results could not be made easily with fixed bed ones because no reaction had been observed in fixed-bed below 900°C. As might have been expected, the extent of reaction at 900°C and 1000°C in the fluidized bed was higher than that obtained with a comparable size range (-72+100 mesh) in the fixed bed at 1100°C. This is no doubt due to the much higher gas velocities needed to keep the fluidized bed in suspension and the more efficient contact achieved between gas and solid in the fluidized state.

It may be seen from the results of Tables 3.1 and 3.2 that there was no obvious large trend in the equilibrium ratios with time of reaction and an average value could be taken. Thus if comparison is made with the fixed bed results this average value can only be compared with the zero-time-extrapolation value. In general it appears that the fluidized bed gives a better approach to theoretical equilibrium than does the fixed-bed.

Gasification of coke with carbon dioxide has been carried out by Gorin and his associates[91] using Disco char and by Gilliland and his co-workers[58] using a high temperature retort coke in a fluidized-bed. The former authors carried out the experiment only at one temperature (871°C) and used only carbon dioxide whereas the latter authors made a comprehensive study with different mixtures of nitrogen and carbon dioxide at different temperatures. The particle size ranges of carbon used in the above cases were -65+150 mesh (T.S.) for Gorin and -20+200 mesh (U.S.S.) for Gilliland. At 800°C the values of equilibrium ratio obtained by Gilliland check very well with the ones reported here, though the solid particle sizes and ratios of inlet gases were somewhat different. The values obtained by Gilliland and Gorin have now been recalculated and incorporated in Figure 3.5, where our experimental values as well as the theoretical values have been compared.

A useful parameter for comparing the N.T.P. average linear velocities in fluidized beds is the lb. moles of gas entering the reactor per minute per square inch of reactor cross-sectional area. We shall call this here the "molar velocity" of the inlet gas. The value may be calculated for Gilliland's results, in which he used approximately 30% carbon dioxide, to be 2.334×10^{-4} lb.moles/min.-in^2, and, for his results using approximately 90% carbon


+8·0
+4·0
-4·0
-8·0
800
1000
1200
1400
T °K
-LOG K_p
THEORETICAL
0 - -100+160 MESH AND 50-60% CO2
× -44+60 " " " " "
+ GILLILAND -20+200 MESH AND 30% CO2
△ " " " 90% "
□ GORIN -65+150 " " 100% "

FIG·3·5

dioxide, to be 2.339×10^{-4} lb.moles/min-in^2. Gorin on the other hand used 100% carbon dioxide at a molar velocity of 1.18×10^{-4} lb.moles/min-in^2. The results of Table 3.1 correspond to an average molar velocity of 2.065×10^{-4} lb.moles/min-in^2 and for Table 3.2 to 1.185×10^{-4} lb.mole/min-in^2. The molar velocities used in the experiments reported here thus fall between the velocities used by Gorin and Gilliland, and hence the results may be safely compared in spite of differences in reactor cross-section. It may be seen from Figure 3.5 that our results agree well with those of Gilliland even although his bed depth (equivalent to about 3.3 lbs fuel in a 1.78 inch I.D. reactor) was much greater than ours (0.7 - 1.45 lbs fuel in a 2 inch I.D. reactor). On the other hand, Gorin who used 1.0 lb fuel in a 1.5 inch I.D. reactor may be seen to have approached considerably nearer to theoretical equilibrium. This indicates that the inherent reactivity of the coke being fluidized, which would be higher for low temperature Disco char, influences the results obtained much more than do the apparatus variables.

It was not possible to operate with the mild steel reactor at higher temperatures than those already reported due both to the limitations of the winding of the electric furnace and to the poor heat resistance of the mild steel tube. After some time of working, the mild steel tube

began to scale severely and the wall became somewhat thin. Since it was hoped to carry out extended gasification studies, it was obvious that a heat resistant stainless steel tube would be required for the reactor. Due to possible contamination of the bed with iron oxide scale from the reactor wall, no gasification studies were made with this reactor in which a bed of carbon on reduced iron was fluidized.

4. FLUID-BED GASIFICATION STUDIES IN STAINLESS STEEL REACTOR

4.1. Apparatus requirements.

To achieve good fluidization in a bed of particles, several possible variables must be carefully controlled. These include reactor dimensions, particle size-distribution of solids in bed, gas velocity and height of bed in reactor.

Unsuitable values for any of the above factors may cause the development of "channeling" or "slugging" in the bed of particles or cause the reactor wall to have an appreciable effect on the process. The smaller the reactor size the greater the effects of these. Hence the ideal fluid-bed characteristics which may be obtained in a large commercial reactor cannot be easily anticipated in a small scale laboratory reactor.

"Channeling", "slugging" and "wall effect" are to a large extent related to the vessel diameter as well as to particle diameter. A large vessel diameter induces the channeling tendency but as one might expect reduces "wall effect". On the other hand, a small diameter tends to promote slugging and "wall effect". The choice of diameter to minimise all these factors must necessarily be a compromise. There are other factors, however, that must limit the diameter of a laboratory reactor. Ease of man-handling the reactor to and from its scaffolding for repair

work, and the need to limit the usage of fluidizing gas to a practical level both prevent large diameter vessels being used. The provision of adequate heating to maintain the reactor at working temperature may involve an excessive electrical load. The available heat must be able to meet the demands of strongly endothermic reactions as well as the normal heat losses from the unit.

Control of reactor temperature, therefore, in the face of the heat demand or evolution of a chemical reaction face of the heat demand or evolution of a chemical reaction heat to be available from the heating system which can be dissipated quickly to waste as necessary, together with the minimum of heat capacity in the reactor body and insulation.

Consideration of the above factors led to the choice of a reactor diameter of about 3 inches, and an electric furnace around the reactor which could be opened to allow rapid dissipation of heat and ease of reactor dismantling.

4.2. Gasification apparatus and ancilliary equipment.

The experimental gasification plant consisted of the following parts:-

(a) Reactor,

(b) Heat supply system,

(c) Gas supply system,

(d) Gas metering devices,

(e) Exit gas cleaning system,

(f) Sampling system,

(g) Gas analysing system,

(h) Pressure measuring instruments.

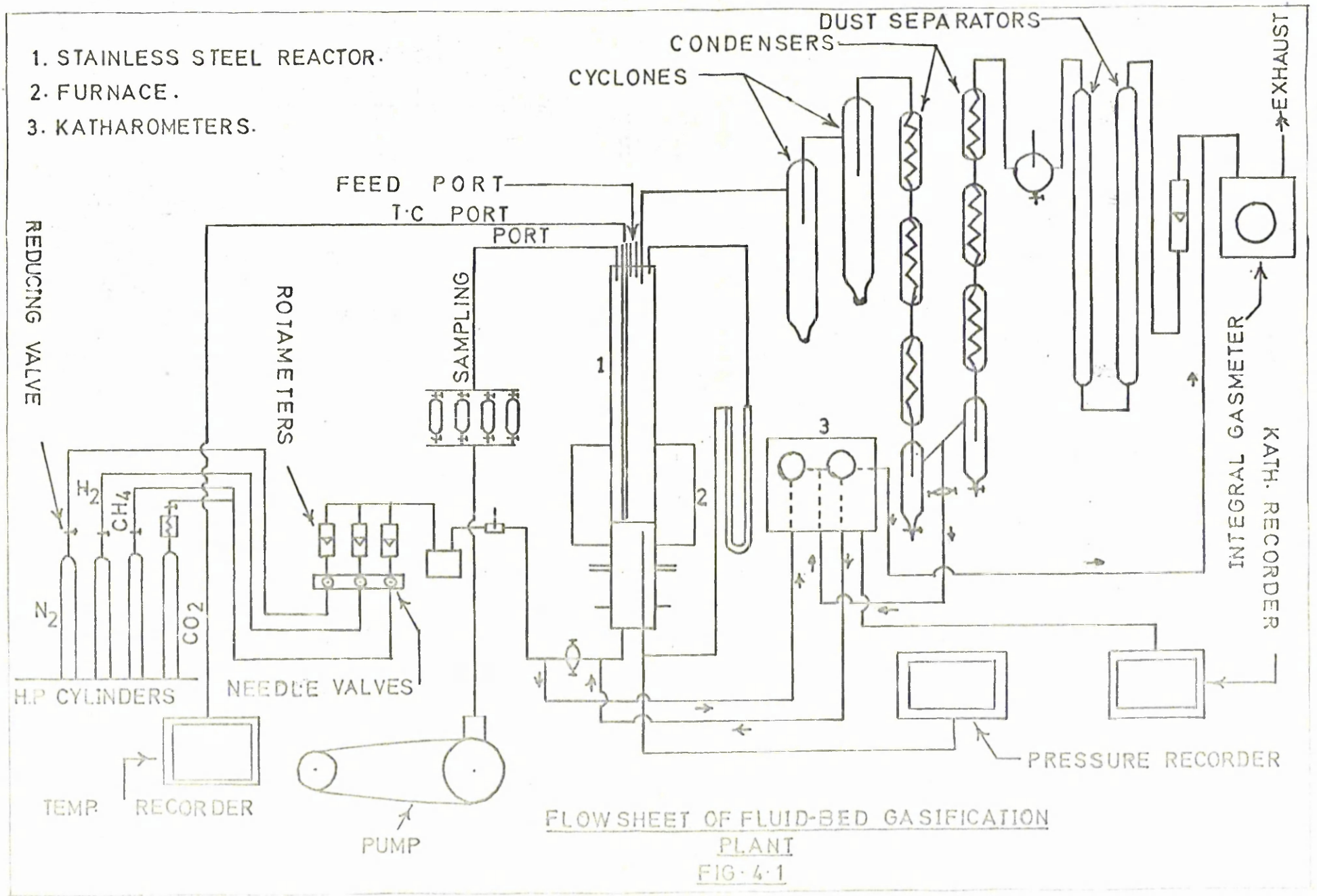
A flow-sheet of the complete plant is given in Figure 4.1 and the plant is illustrated in Photograph No.1.

4.2.1. Stainless steel reactor. The reactor was constructed from two lengths of stainless steel tubing (AISI type 316). These were :-

(a) a 5 ft length 3 inch O.D. (wall thickness = 0.125 inch),

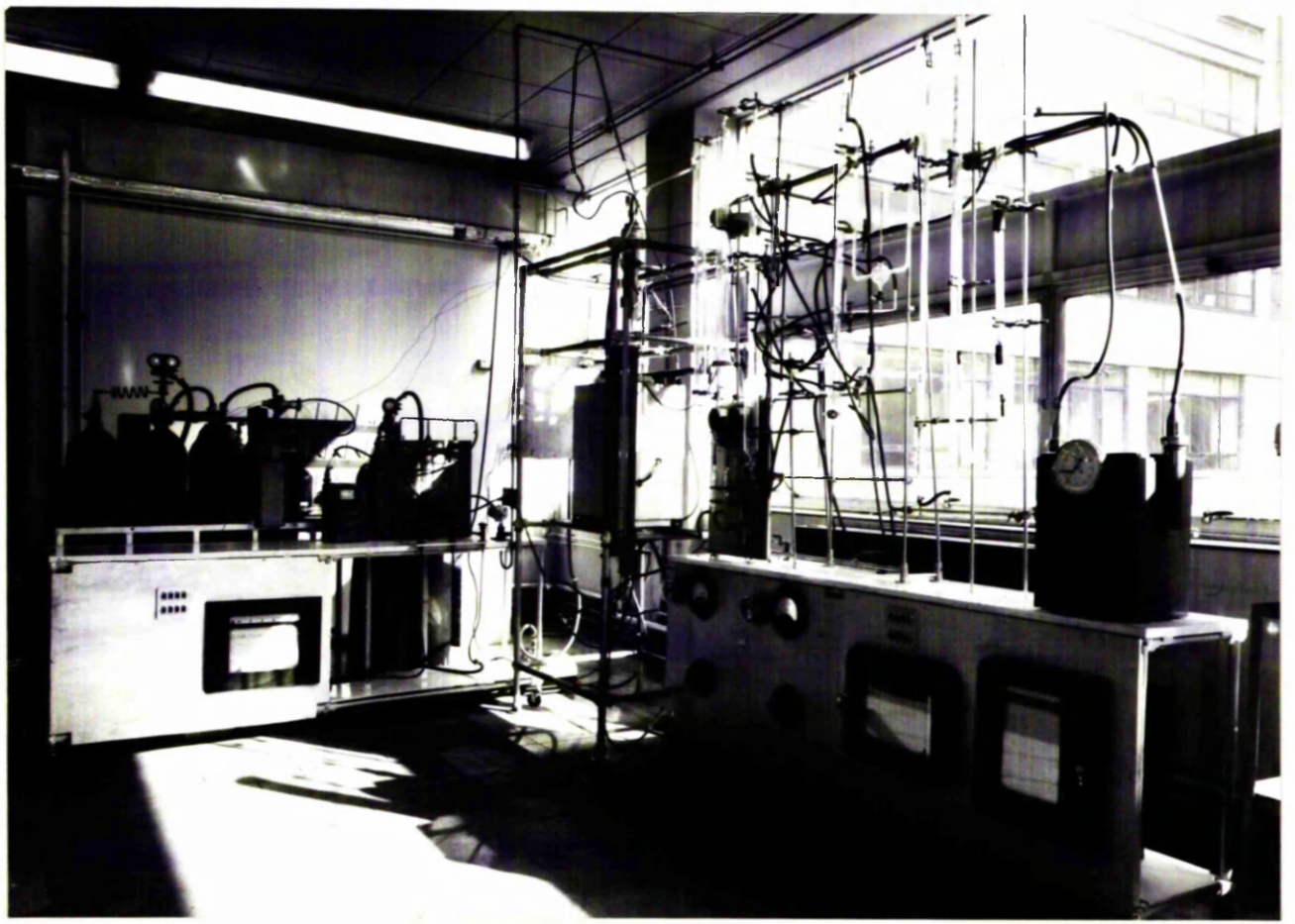
(b) a 15 inch length of $2^3/4$ inch O.D. (wall thickness = 0.128 inch).

The larger length had a flange fitted to one end and 10 inches of the inner surface of the tube from this flange was lightly machined, as was the same length of the outer surface of the smaller diameter tube. The smaller tube was fitted with a flange 10 inches from its end (at the point where the machining stopped). The smaller diameter tube could then be slid into the larger until the two flanges met. The flanges were grooved to take an O-ring of neoprene rubber. The overall clearance between the tube was 0.04 inch for the first 5 inches from the flange and 0.4 thousandths of an inch for the remaining 5 inches. A disc of 1/8 inch thick porous stainless steel (2.76 thousandths of an inch mean pore size) was firmly seated



FLOW SHEET OF FLUID-BED GASIFICATION PLANT

FIG·4·1



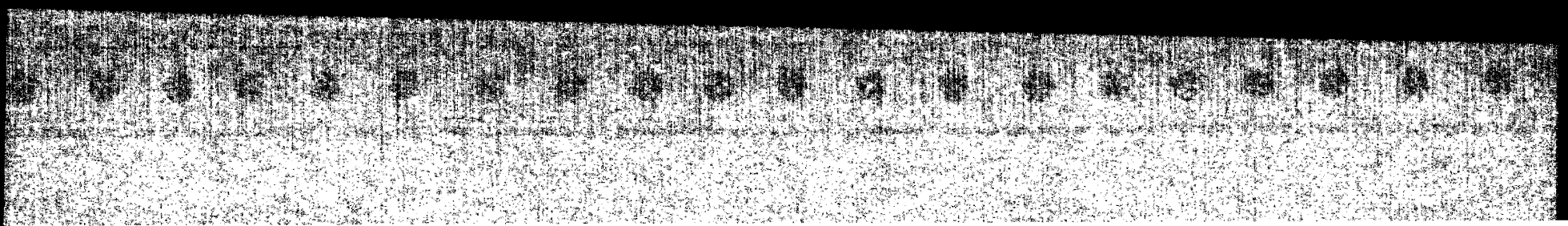
Photograph No.1. Laboratory Gasification Plant

in a groove cut in the top end of the inner tube. In use the larger tube was clamped vertically in a tubular steel scaffolding framework with its flange at the lower end. The inner tube was then slid into it from the bottom and the two flanges bolted together. Removal of the inner tube, on loosening the bolts, was facilitated by a pair of steel handles welded to it below the flange. The arrangement of the tubes which form the reactor is shown in Figure 4.2.

Two cooling coils of 1/4 inch I.D. copper tubing were wound around and brazed to the larger tube just above the flange to protect the O-ring, and the other near the top of the tube which was itself closed by a neoprene rubber stopper. The underside of this stopper (facing the hot fluid-bed) was protected by a 1/4 inch thick asbestos sheet cut to the size of the narrow end of the stopper and screwed to it by self-tapping screws. This stopper and asbestos protecting plate were pierced by five holes through which passed

(a) a 5 ft length of 1/4 inch I.D. silica tubing with a closed lower end which rested on the upper side of the sintered disc. This silica tube served as a thermocouple pocket,

(b) a short length of 12 mm diameter glass tube closed at the top by a B19/26 ground joint glass stopper. This served as a feed port for solids,



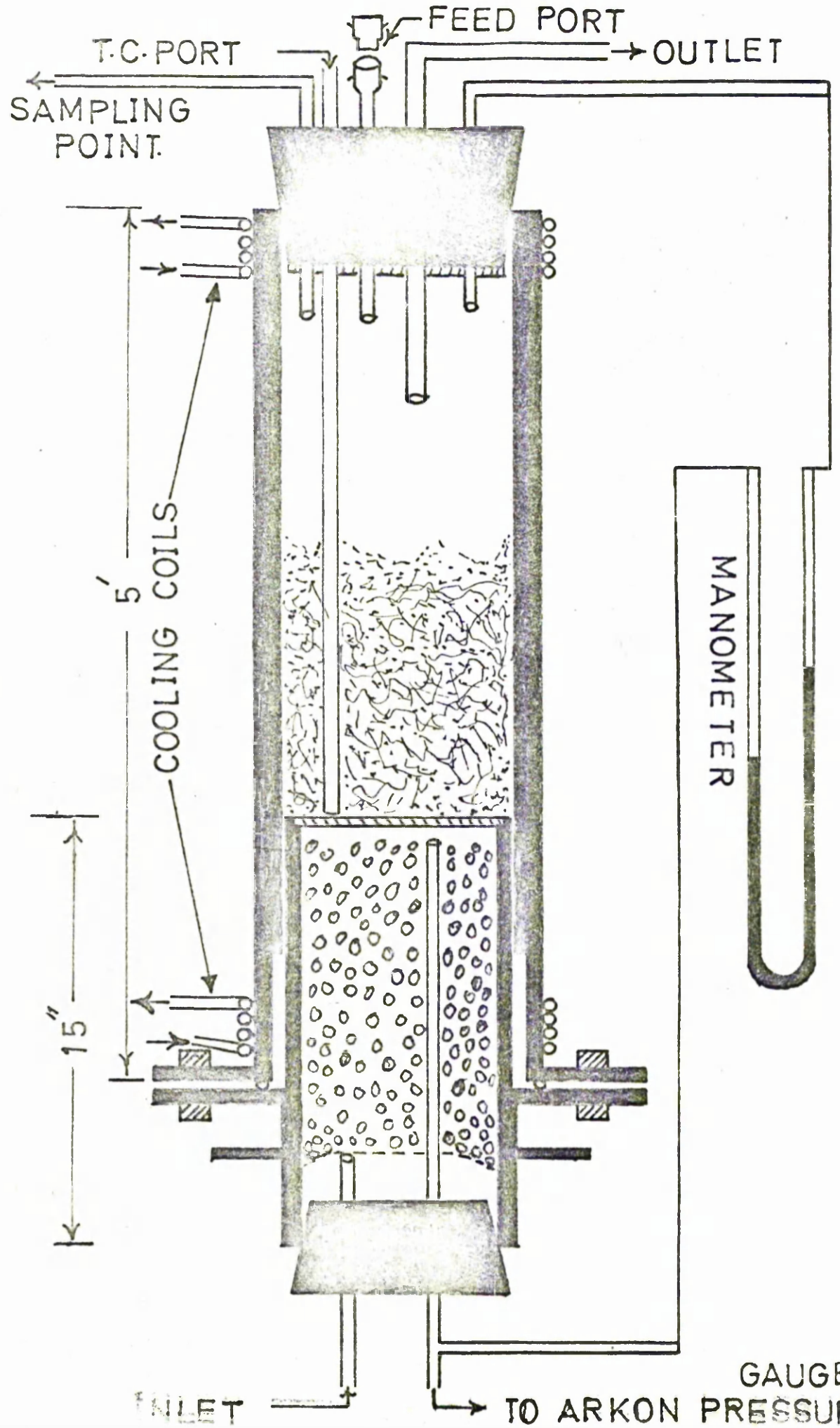

FEED PORT
T.C. PORT
OUTLET
SAMPLING POINT
5'
COOLING COILS
MANOMETER
15"
INLET
GAUGE
TO ARKON PRESSURE

FIG-4.2

(c) the exit gas line of 18 mm O.D. tubing with about 6 inches of its length extending into the reactor,

(d) a 6 mm O.D. glass tube which extended 5 inches into the reactor. This tube was connected to the gas sampling system,

(e) a 6 mm diameter glass tube connected to the manometer measuring the pressure drop across the porous plate and the fluidized bed.

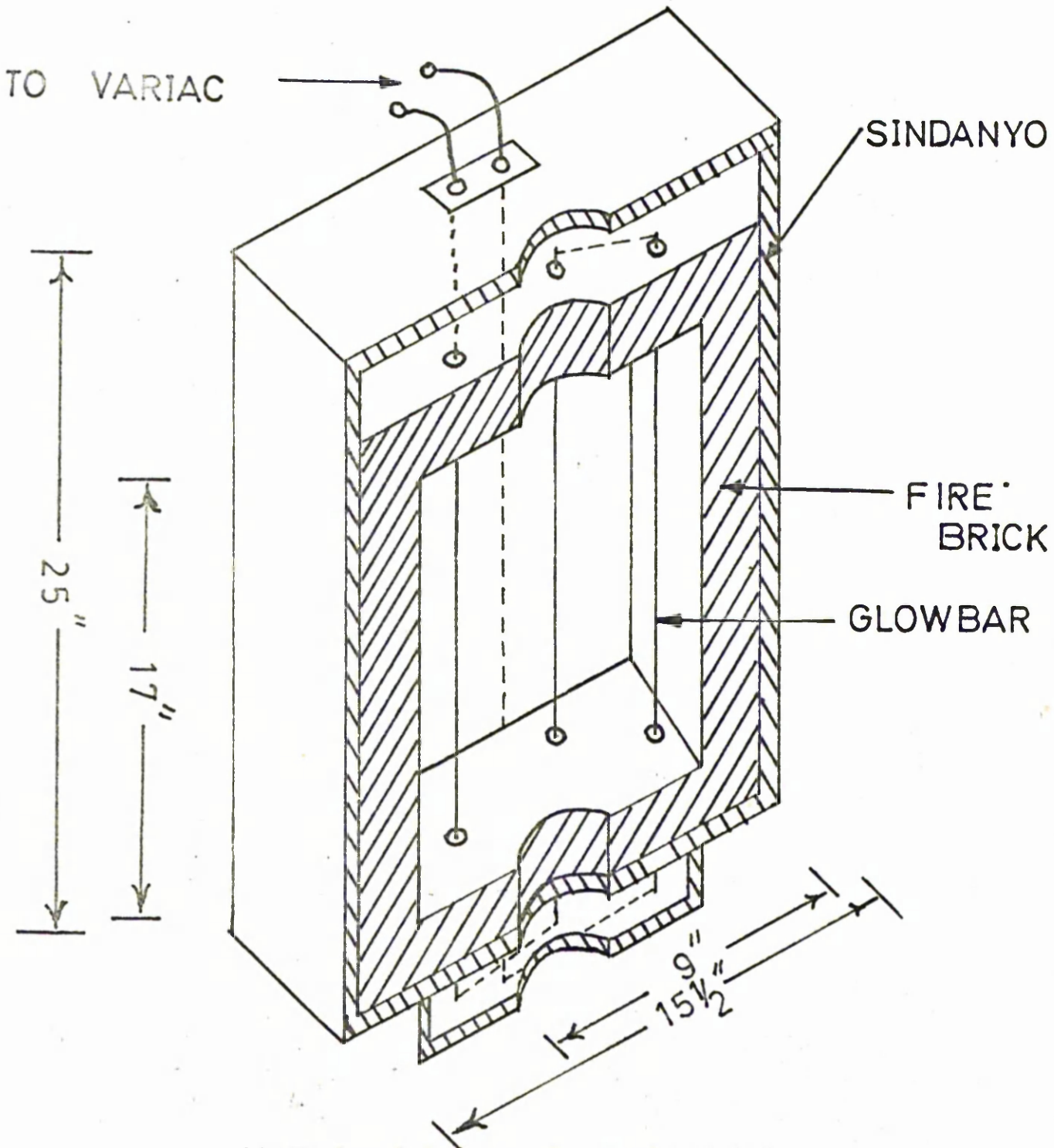
The interior of the smaller stainless steel tube was almost completely filled with ½ inch diameter alundum balls. They were supported by a dome-shaped piece of stainless steel wire gauge and a rubber stopper which was fitted into the lower end of the tube. This stopper was pierced by two metal tubes. One was a copper tube of 1/4 inch I.D. which served as gas inlet point and the other was a 1/4 inch O.D. (wall thickness = 0.036 inches) stainless steel tube which extended up close to the underside of the porous disc and served as a pressure tapping. The alundum balls were intended to aid in the preheating of the inlet gases. A Chromel-Alumel thermocouple connected to a Honeywell-Brown electronic recorder was fitted into the silica pocket.

4.2.2. Heat supply system. Heat to the reactor was provided by a specially designed box furnace which fitted around it. The furnace was composed of two separate and completely independent halves which moved horizontally on

rails and rollers. The two halves could be closed together around the reactor or pulled apart easily to allow the reactor to cool quickly or to facilitate its removal from the scaffolding.

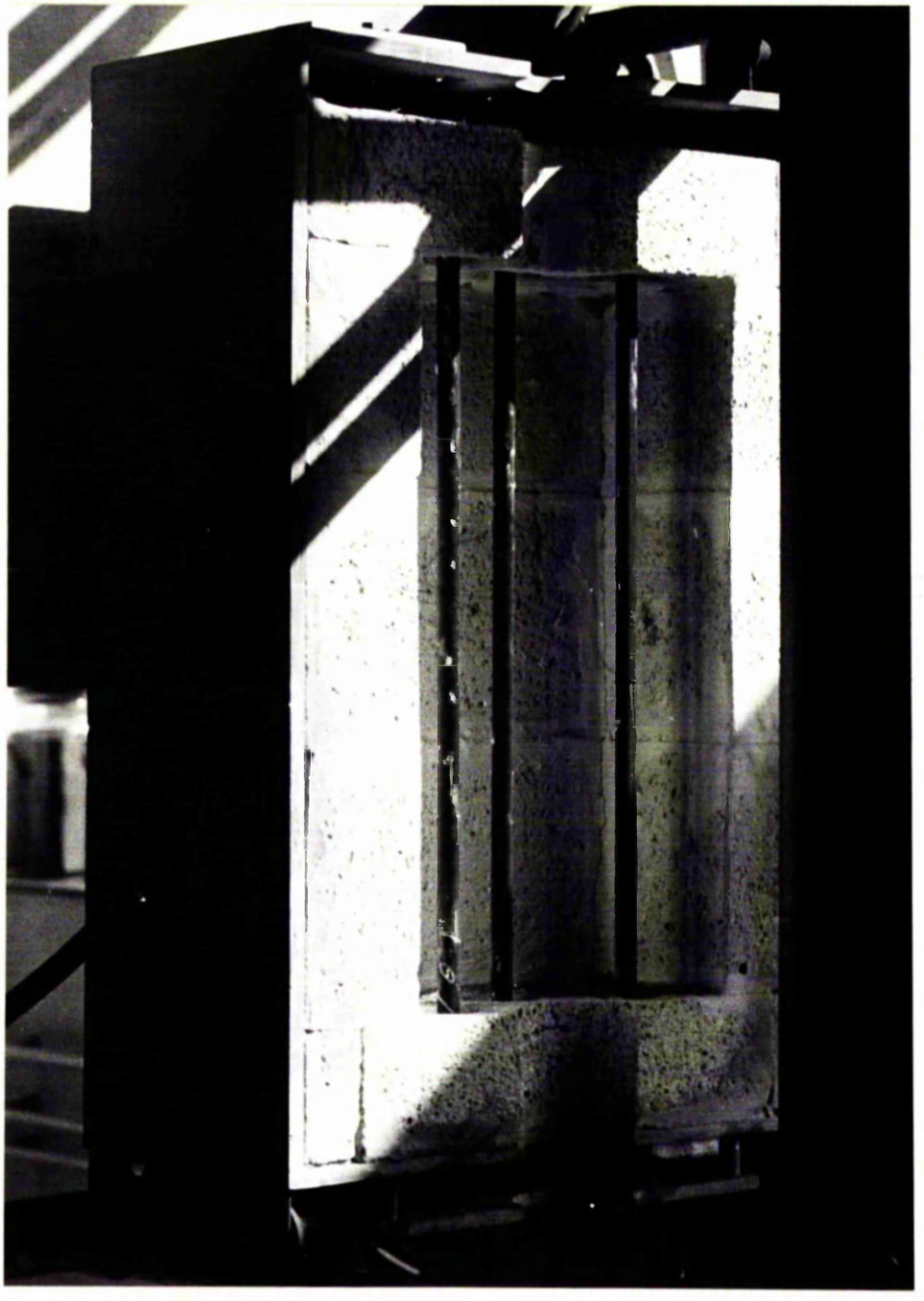
Each half of the box furnace was fabricated from ½ inch thick Sindanyo lined with 3 inch thick firebrick, and contained three "Glowbar" heating elements (½ inch diameter and 25 inches long), each with a nominal resistance of 3.6 ohms mounted in series. Current was supplied to the elements via a 20 amp synchronous time switch, "Variac", and ammeter. When the box furnace was closed around the reactor it was able to heat a length of 17 inches. To maintain the reactor at, say, 1300°F required a current of about 11.5 amperes to each half of the box-furnace. A view of one half of the furnace is given in Figure 4.3. It may also be seen in Photograph No.2. and No.3.

4.2.3. Gas supply system. The gases used were supplied from seven standard high pressure cylinders. Cylinders each of hydrogen, nitrogen and methane gas were joined in pairs by couplings to ensure a continuous gas supply over prolonged periods of operation. A cylinder providing liquid carbon dioxide was used and this was fitted with a suitable vaporisor.

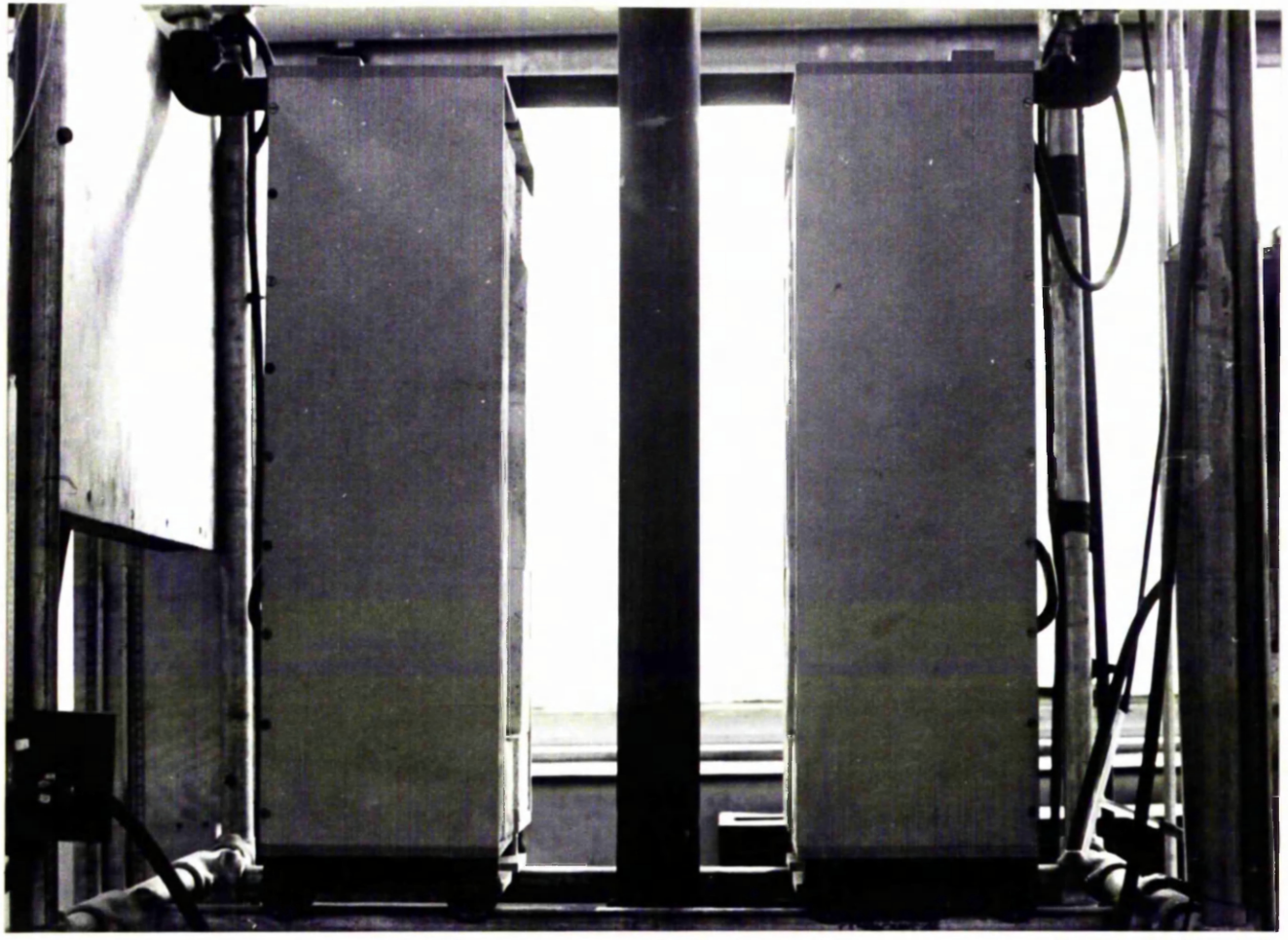


VIEW OF HALF FURNACE

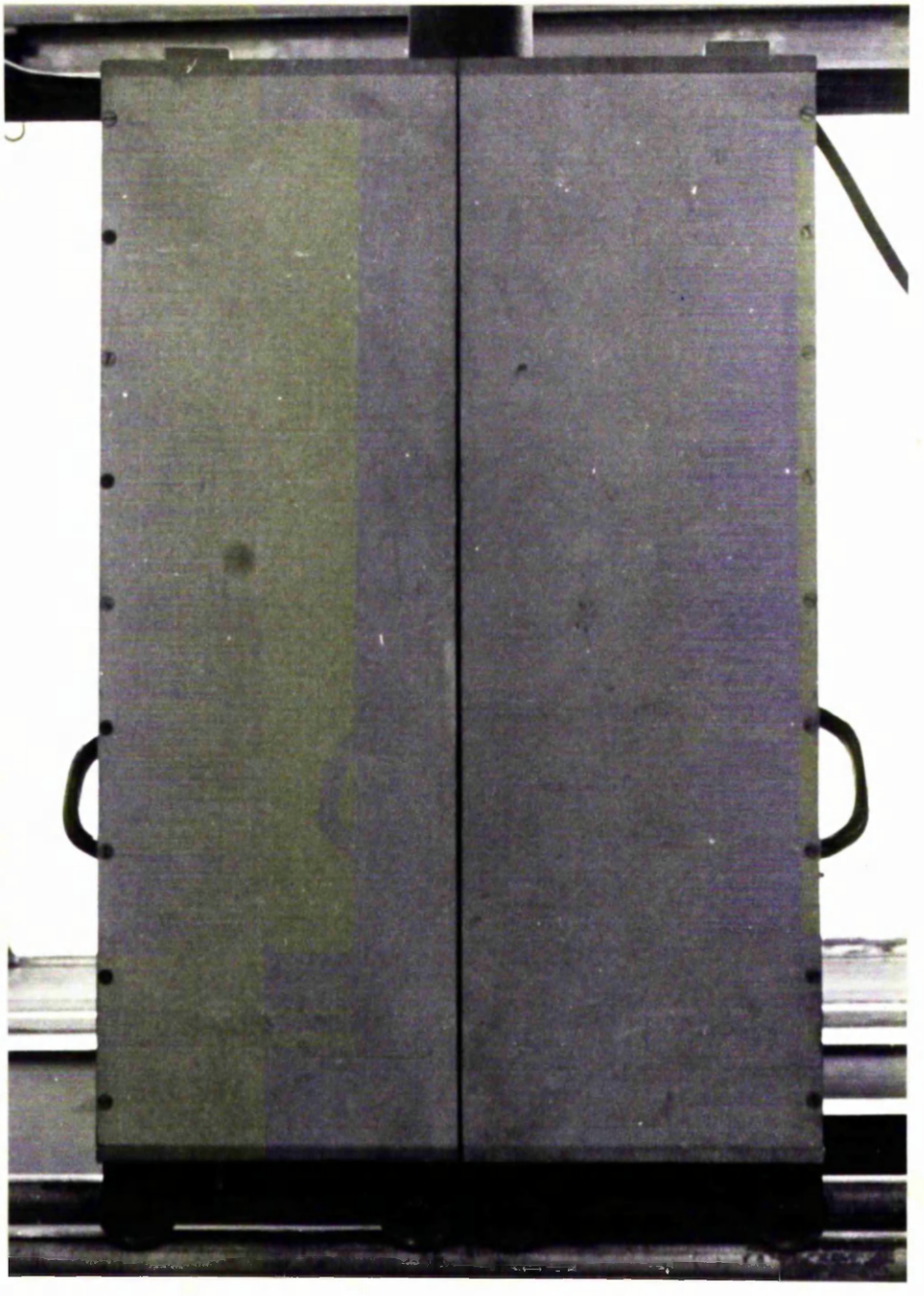
FIG·4.3



Photograph No.2. View of half-furnace used to heat stainless steel reactor



Photograph No.3. View of furnace in "open" position



Photograph No.4. View of furnace in "closed" position

The gas flows were doubly controlled before entering the reactor. First by the reducing values fitted to the tops of the cylinders and then by needle valves. This system gave a wide range of control of the flowrates.

4.2.4. Gas metering instruments. The individual flowrates were indicated on standard rotameters and an integral conventional dry gasmeter was used to indicate the overall gas flow. The temperature of the inlet gas-stream was indicated by a thermometer inserted in the main line. Provision was also made to supply compressed air from the laboratory supply to the reactor. After cleaning and cooling, the outlet gas flow was metered through a rotameter first and then through a dry test integral gasmeter. The benefit of the inclusion of the rotameter in the outlet line was that it gave an indication of leakage from the system and also a rapid vibration of the rotameter float was found to be a good indicator of the condition of fluidization in the reactor. Another thermometer was inserted in the outlet gas stream after the condensers to indicate outlet gas temperature.

The rotameters in the feed lines were calibrated for each particular gas by use of dry test meters.

4.2.5. Exit gas cleaning system. The product gases from the reactor first passed through two cyclones placed in

series where any coarse particles carried over were separated. Then the stream entered the condensing system which comprised two columns each of three spiral glass condensers, each column being provided with a water receiver. The product gases then entered two dust filter tubes packed with glass wool. The cleaned cooled gas then passed to the gas meter and then to waste.

4.2.6. Gas sampling system. To enable snap samples of the exit gas to be collected at will, four B.S. 250 ml gas sampling bulbs provided with three-way stop-cocks at each end were connected to a manifold and mercury manometer at one side and a manifold and vacuum pump at the other. The whole system could connect to the glass sampling line passing into the gas space of the reactor. Another stop-cock was provided on this line to allow the vacuum system to be isolated from the reactor. In use the vacuum pump was used to evacuate the sample bulbs to a pressure indicated on the mercury manometer. When it was desired to collect a snap sample the cocks were turned to link an evacuated gas bottle to the reactor.

4.2.7. Gas analysing system. At the beginning of this part of the work gas analysis was done by conventional means, viz. absorption and combustion methods. It was soon found, however, that the analysis time limited the number of gas samples that could be collected during a run.

Later analysis was done on a Perkin Elmer (model 452) gas chromatograph using a silical gel column.

It was finally decided that "snap" gas samples could not give the required information about the gasification process and that a continuous record of the outlet gas composition should be obtained. This was achieved by means of two Katharometers supplied by the Cambridge Instrument Company.

These were as follows :-

(a) a square block direct-acting katharometer previously calibrated to measure 0 - 100% carbon dioxide in nitrogen,

(b) a differential carbon dioxide katharometer also calibrated with 0 - 100% carbon dioxide in nitrogen.

In operation the inlet gas was passed through both (a) and (b) and the outlet gas from the reactor through (b) only. The signal from each katharometer was fed to a common recorder where two pens recorded the readings simultaneously. The principles of the arrangement and the means of calculating the exit-gas analysis from it are discussed in section 4.6 later.

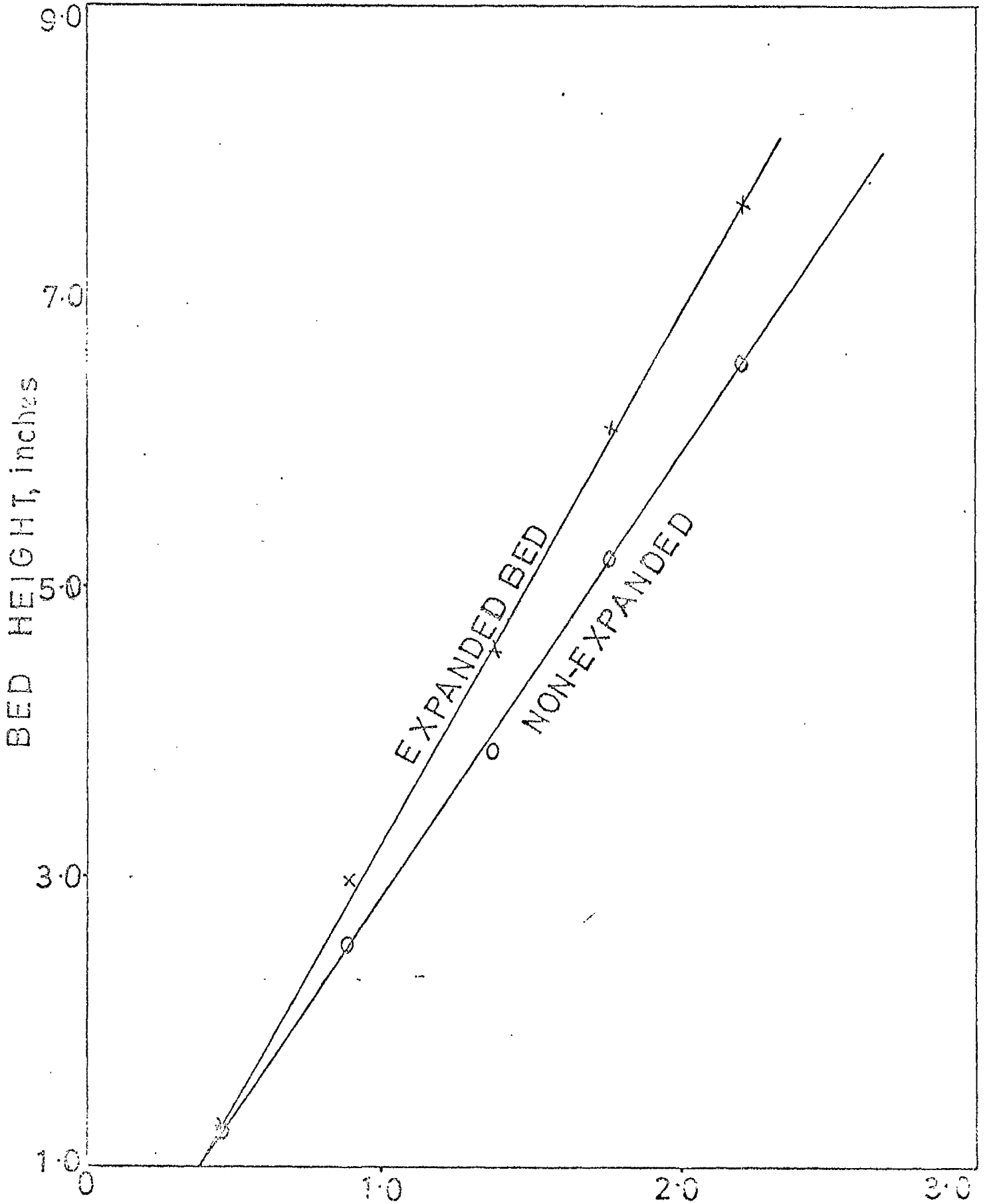
4.2.8. Fluid-bed pressure measuring equipment. The pressure-drop across the bed of particles in the reactor was measured by a mercury manometer, one end of which was

connected to the stainless steel pressure tapping under the porous disc in the reactor and the other end to the top of the reactor. In practice, the fluctuation of the mercury level in the manometer gave an excellent indication of the state of fluidization of the bed of particles.

A diaphragm type Arkon strip-chart pressure-recorder (model 1600) with a range of 0 - 60 inches water gauge, was connected to the stainless steel pressure tapping through a T-junction. The chart speed used was 12 inches per hour. The instrument really recorded the inlet pressure of the fluidizing gas and gave a valuable indication of any progressive development of trouble in the fluidized bed.

4.3. Expansion characteristics of fluid-bed.

Before assembling the reactor, it was decided to measure the expansion characteristics of the bed of iron ore when completely fluidized. This was studied by replacing the main body of the reactor by a 3ft length of glass tubing of $2\frac{3}{4}$ inch I.D. This was fitted over the stainless steel inner tube and the joint between the steel tube and the glass tube was sealed with P.V.C. tape. Several beds of different weights of iron ore were fluidized in this glass-bodied reactor and the heights of the original as well as expanded beds above the porous disc were measured. The results are plotted in Figure 4.4.


9·0
7·0
5·0
3·0
1·0
0
1·0
2·0
3·0
BED HEIGHT, inches
EXPANDED BED
NON-EXPANDED
ED WEIGHT, lbs

FIG·4·4

These tests also furnished an opportunity for a visual observation of the possible future fluid-bed behaviour of the particulate material under consideration.

4.4. Temperature distribution in the reactor.

To determine temperature profile of the reactor, two experiments were carried out in which future experimental conditions were simulated. 1.76 lbs (800 gms) of iron ore were placed in the reactor on the porous plate and the bed was completely fluidized. The temperature of the reactor was brought to a predetermined value and held at this value during the whole operation. The thermocouple was set at different positions in its pocket along the length of the reactor and a temperature measurement taken after a ten minute interval. Average bed temperatures chosen for this purpose were 1200°F and 1400°F, with an unexpanded bed height of 5.2 inches and an expanded height of 6.1 inches. Figure 4.5 shows the temperature distribution along the length of the reactor and indicates that the temperature throughout the fluidized bed was virtually constant.

4.5. Pressure-drop-flow diagrams for fluidized bed.

As already stated, an excellent indication of the fluidization behaviour of a granular material may be obtained from the pressure-drop-flowrate relationships of the expanded bed. Measurements were accordingly made with several initial bed weights to determine the fluidization characteristics of

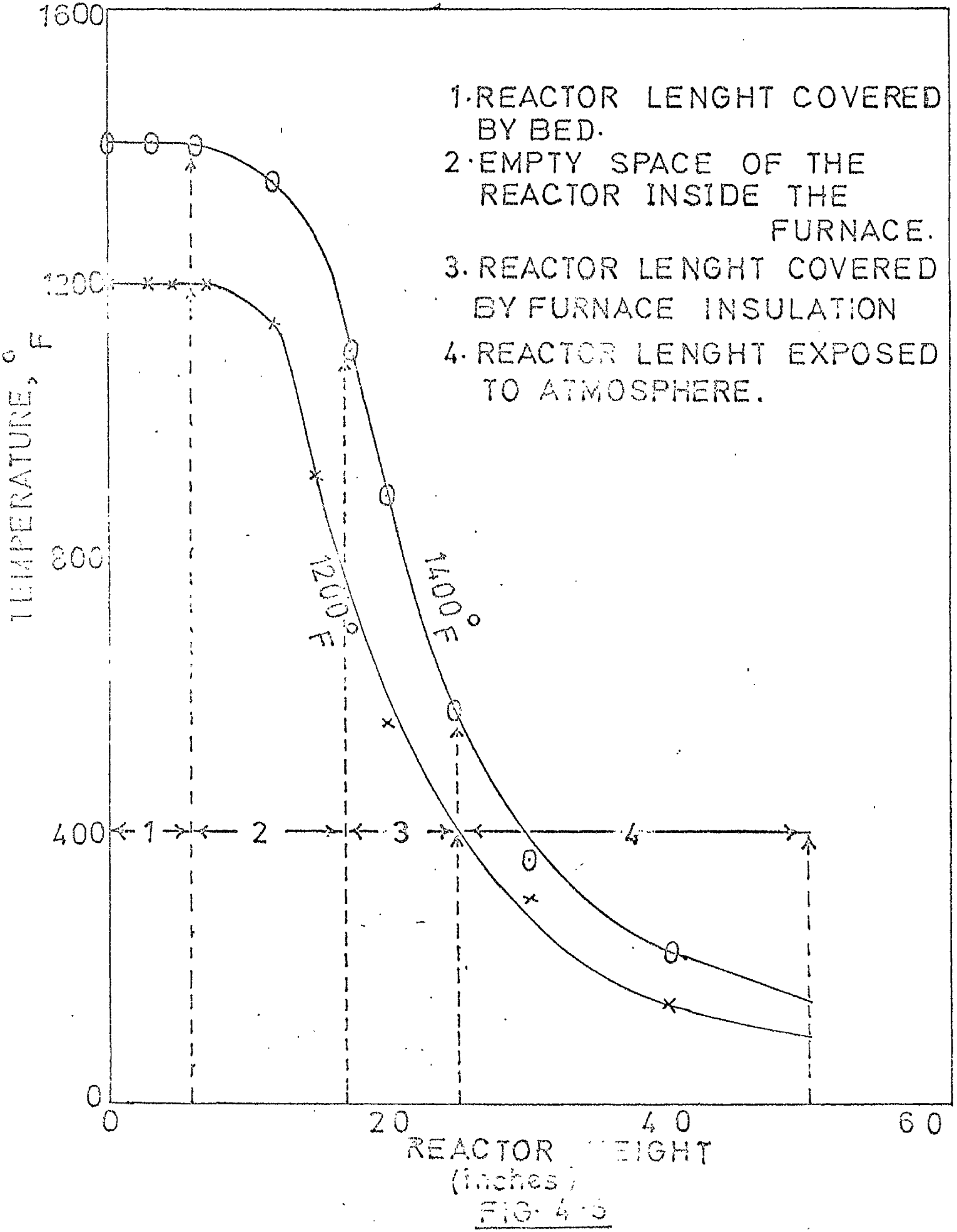

1600
1200
800
400
0
TEMPERATURE, °F
1. REACTOR LENGHT COVERED BY BED.
2. EMPTY SPACE OF THE REACTOR INSIDE THE FURNACE.
3. REACTOR LENGHT COVERED BY FURNACE INSULATION
4. REACTOR LENGHT EXPOSED TO ATMOSPHERE.
1400° F
1200° F
1
2
3
4
0
20
40
60
REACTOR HEIGHT
(Inches)

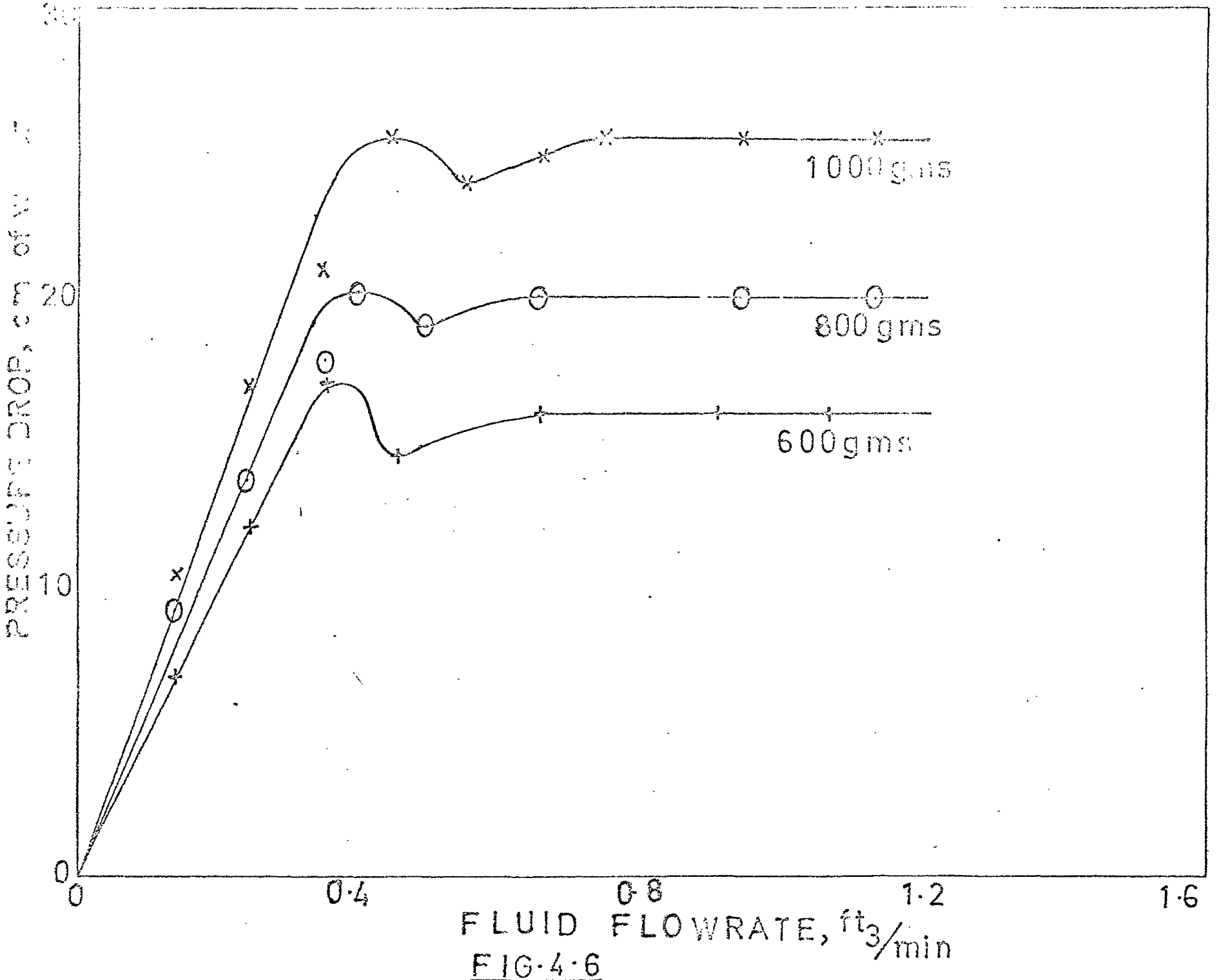
FIG. 4-5

the -52+100 mesh B.S.S. particle size range of iron ore. Pressure-drop-flow diagrams are given in Figure 4.6. The diagrams indicate that the beds were well fluidized, at a fluidizing gas flowrate of 0.8 ft^3/min. This corresponded to a superficial linear velocity of 0.323 ft/sec. The measured pressure-drops were found to agree well with that calculated from the weight of material in the bed and reactor internal diameter. Table 4.1 compares the calculated pressure drops with the measured values.

sured pressure

TABLE 4.1 Comparison of calculated with measured pressure drops in fluidized-beds of iron ore.

Bed weight		Pressure-drop, ΔP, (cm of water)	
lbs	gms	Calculated	Measured
1.32	600	16.25	15.90
1.76	800	20.80	20.00
2.20	1000	26.02	25.60


PRESSURE DROP, cm of W
30
20
10
0
1000 gms
800 gms
600 gms
0
0·4
0·8
1·2
1·6
FLUID FLOWRATE, ft3/min

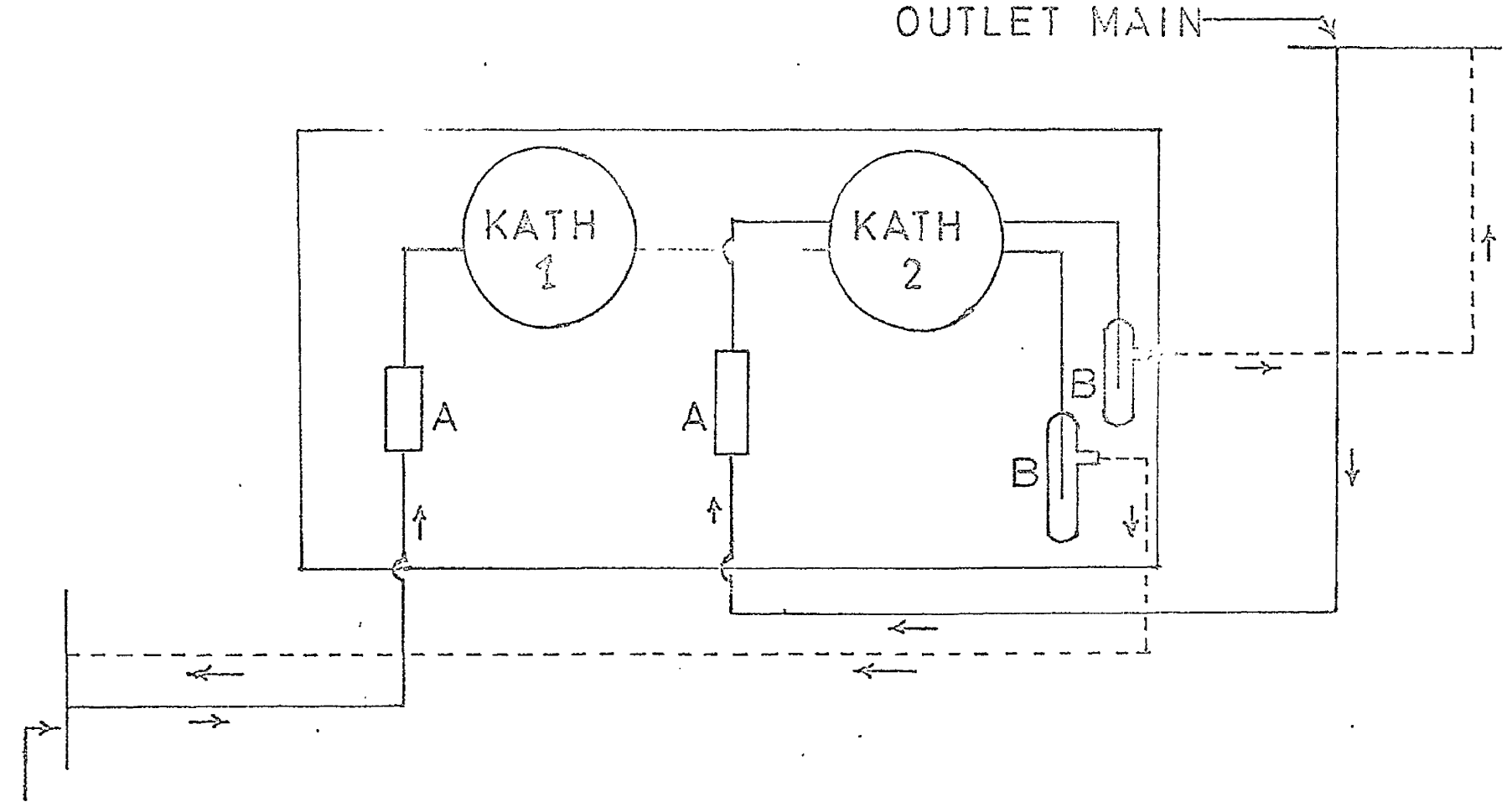
FIG·4·6

4.6. Calculation of off-gas analysis.

4.6.1. Arrangements of Katharometers. It was earlier stated that the off-gases were analysed by means of two katharometers, viz. (a) direct acting, and (b) a differential one. The arrangement of these meters in the reactor system is shown in Figure 4.7.

They were connected to the inlet gas stream through a T-junction and a small fraction of the inlet gas was diverted to the katharometers by a screw clip on the main gas inlet line. A small calcium chloride trap was placed in the sample line before the katharometers to remove any moisture in this fraction of the inlet gas and the flowrate was controlled to 200 - 250 c.c/min by a miniature glycerine filled flowmeter placed in the line after the katharometers. The sample gas was then returned to the main inlet flow line at a point down-stream just prior to entry to the reactor. In the same way, a sampling line carried outlet gas from the condensers to the differential katharometer and returned it to the main exit stream just before the final integral gas meter. The sample line lengths were arranged so that as far as possible the differential katharometer was comparing inlet and outlet gases corresponding to the same point in time.

4.6.2. Principles of Katharometer measurement. The measurement of the composition of a gas mixture by a katharometer is based on gas thermal conductivity. The katharometer contains four platinum wires with identical thermal and electrical characteristics which are enclosed



A. CALCIUM CHLORIDE TRAPS.
B. MINIATURE FLOWMETERS.

FIG. 4.7 ARRANGEMENT OF THE KATHAROMETERS.

in separate cells in a solid metal block. Each wire forms one arm of a Wheatstone bridge. A constant current is fed into the bridge thereby raising the temperature of the wires which then lose heat to their surroundings. If two gases having different thermal conductivity are introduced each into a pair of cells, there will be a difference in the extent of cooling of the wires and, therefore, a difference in the electrical resistance. This will throw the bridge out of balance causing a deflection on a suitably arranged galvanometer. This deflection becomes a measure of the difference in composition of the gases being compared.

The instrument may be calibrated by the use of pure gases or mixture of known composition.

4.6.3. Principles of gas composition calculation. The inlet gas for the gasification of carbon in the reactor was a mixture of carbon dioxide and nitrogen. The method of calculating the exit gas analyses (i.e. percentages of carbon dioxide, carbon monoxide and nitrogen) from the katharometer readings was as follows :-

Basis ..... 100 moles of inlet gas.

Let moles of carbon dioxide in inlet gas = x

then moles of nitrogen = 100 - x

Let moles of carbon dioxide converted to carbon monoxide in reaction = y

Thus in the outlet gas there will be :-

Carbon dioxide	=	(x - y) moles
Carbon monoxide	=	2 y moles
Nitrogen	=	100 - x moles
Total	=	100 + y

The equation for the reaction is :-

$$x\ CO_2 + (100 - x)\ N_2 = (x - y)\ CO_2 + 2y\ CO + (100 - x)\ N_2$$

One side of the differential katharometer is exposed to the inlet gas which will contain $\frac{100\ x}{100}$ %, i.e. x per cent carbon dioxide, and the other to :-

$\frac{100(x - y)}{(100 + y)}$ per cent carbon dioxide plus $\frac{200\ y}{100+y}$ per cent carbon monoxide.

The meter reading is then the difference between these two gas mixtures when the second has been converted to an equivalent reading of carbon dioxide in nitrogen. This equivalent is :-

$$Z = \frac{100(x-y)}{(100 + y)} + k_1 \frac{(200\ y)}{(100+y)} .$$

The introduction of the factor k_1 is necessary since the meter has a different sensitivity to carbon monoxide to that of carbon dioxide, e.g. if a gas consisting of one per cent carbon dioxide in nitrogen gives a deflection of one unit on the meter, a gas consisting of one per cent carbon monoxide in nitrogen would only give a reading of about

0.15 units.

The value of the factor k_1 depends on the carbon dioxide concentration and increases from about 0.11 to 0.15. The overall relationship[93] for k_1 is as follows :-

$$k_1 = 0.113 + 0.06\frac{(x - y)}{(100 + y)}$$

A further correction must be made for the curvature of the recorder scale, since the reading given by 20% carbon dioxide against nitrogen is not quite the same as that for 100% carbon dioxide against 80% carbon dioxide. Data for the preparation of a scale shape curve were provided by the Cambridge Instrument Company Limited and this curve has been drawn in Figure 4.8.

If the differential katharometer is used with gas "before reaction" on one side and the gas "after reaction" on the other side, the output from this katharometer is the difference between the outputs due to x % CO_2 and Z "% CO_2". Let the reading given by this katharometer be q "% CO_2". To find Z the necessary correction must be obtained from the "scale shape" curve provided.

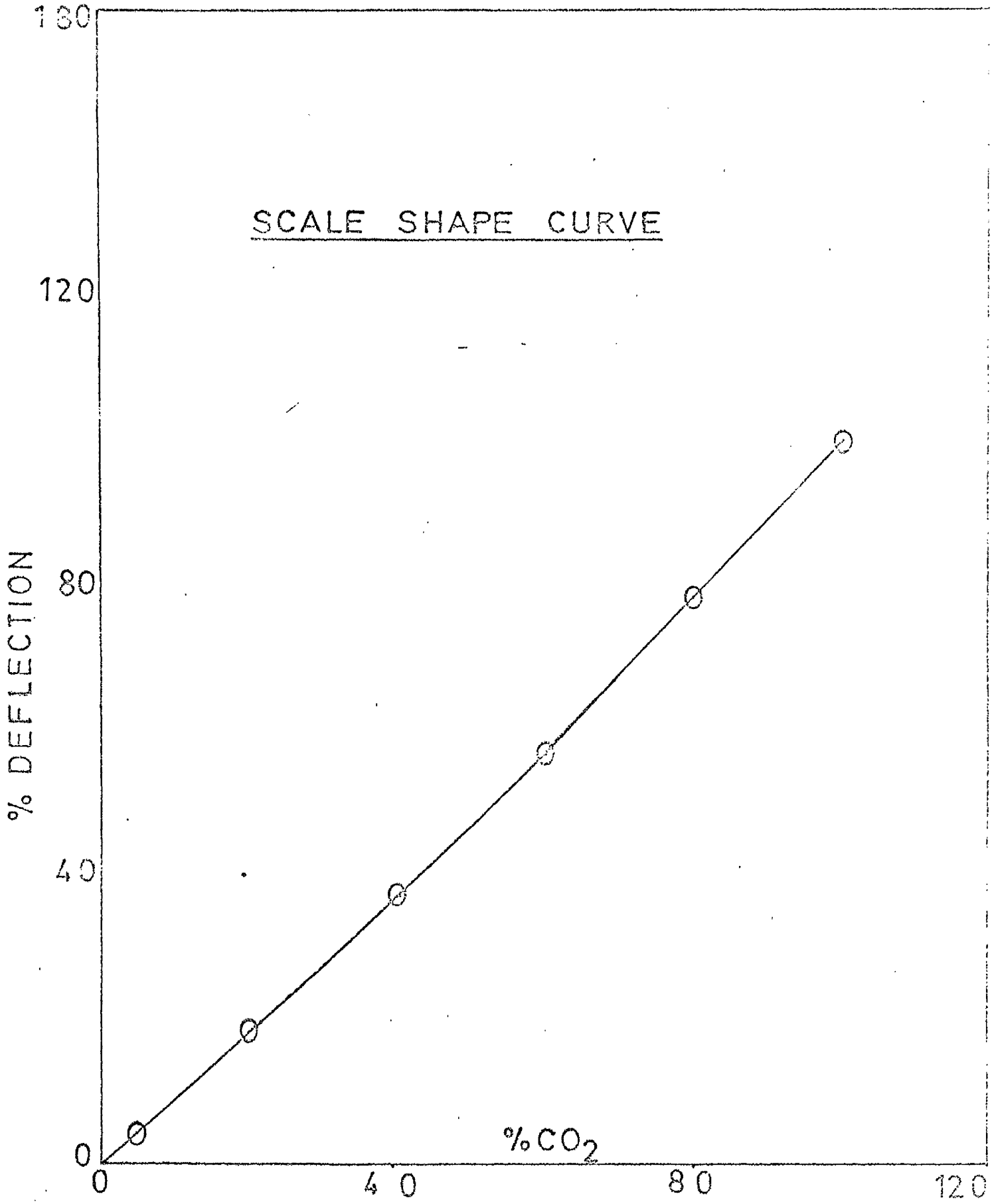
Example: From the scale shape curve, find the deflection that corresponds to $x(= d_1)$ and that due to $q(= d_2)$. Find the CO_2 percentage equivalent to $(d_1 - d_2)$. This gives Z.

e.g. From the direct acting katharometer,

$x = 70\%\ CO_2$ $\quad\therefore\quad d_1 = 67.5$

From the differential katharometer,

$q = 40\%\ CO_2$ $\quad\therefore\quad d_2 = 37.2$



FIG·4·8

$\therefore\ d_1 - d_2 = 67.5 - 37.2 = 30.3$

and this, from the scale shape curve, corresponds to

32.8% carbon dioxide = Z.

To evaluate y from these values of x and Z, one employs the equation:-

$$Z = \frac{100(x - y)}{(100 + y)} + \left[0.113 + 0.06\,\frac{(x - y)}{(100+y)}\right]\frac{200\ y}{100+y}$$

$$= \frac{100(x - y)}{100 + y} + 200y\,\frac{(113 + 0.06x + 0.053y)}{(100 + y)^2}\ .$$

The solution of this equation for a given value of x and Z will be most time consuming. Perhaps the best approach was found to be the selection of values of y at a suitable value of x and the evaluation of Z.

Say, that in a test run, x = 54.5% CO_2

Let y = 10, 20, 30, ... etc.

e.g. for y = 10,

$$\frac{100(x - y)}{(100 + y)} = \frac{100(44.5)}{110} = 40.4$$

$$\frac{200\ y}{100+y} = \frac{2000}{110} = 18.18$$

$\therefore\ k_1 = 0.113 + 0.06(40.4)$

$= 0.113 + 0.242 = 0.355$

$\therefore\ Z = 40.4 + 0.355(18.18)$

$= 40.4 + 6.45 = 46.45\%\ CO_2$

From the scale shape curve, this value of Z corresponds to $d_1 - d_2 = 43.8$ and again from the scale shape curve when

$$x = 54.5\%\ CO_2 , \qquad d_1 = 51.5$$

$$\therefore \quad d_2 = 51.5 - 43.8 = 7.7$$

Then, from curve, $q = 8.5\%\ CO_2$.

If this technique is repeated for other selected values of y, a curve may be drawn. Such curves were drawn in Figure 4.9 for x = 20, 30, 40, 50, 60, 80 and 100 per cent carbon dioxide as recorded by the direct-acting katharometer. From these curves, the values of q ("per cent of carbon dioxide" given on the chart by the pen on the recorder related to the signal from the differential katharometer) may be related to y and the gas analysis calculated therefrom.

<u>Sample calculation of gas analysis using Figure 4.9.</u>

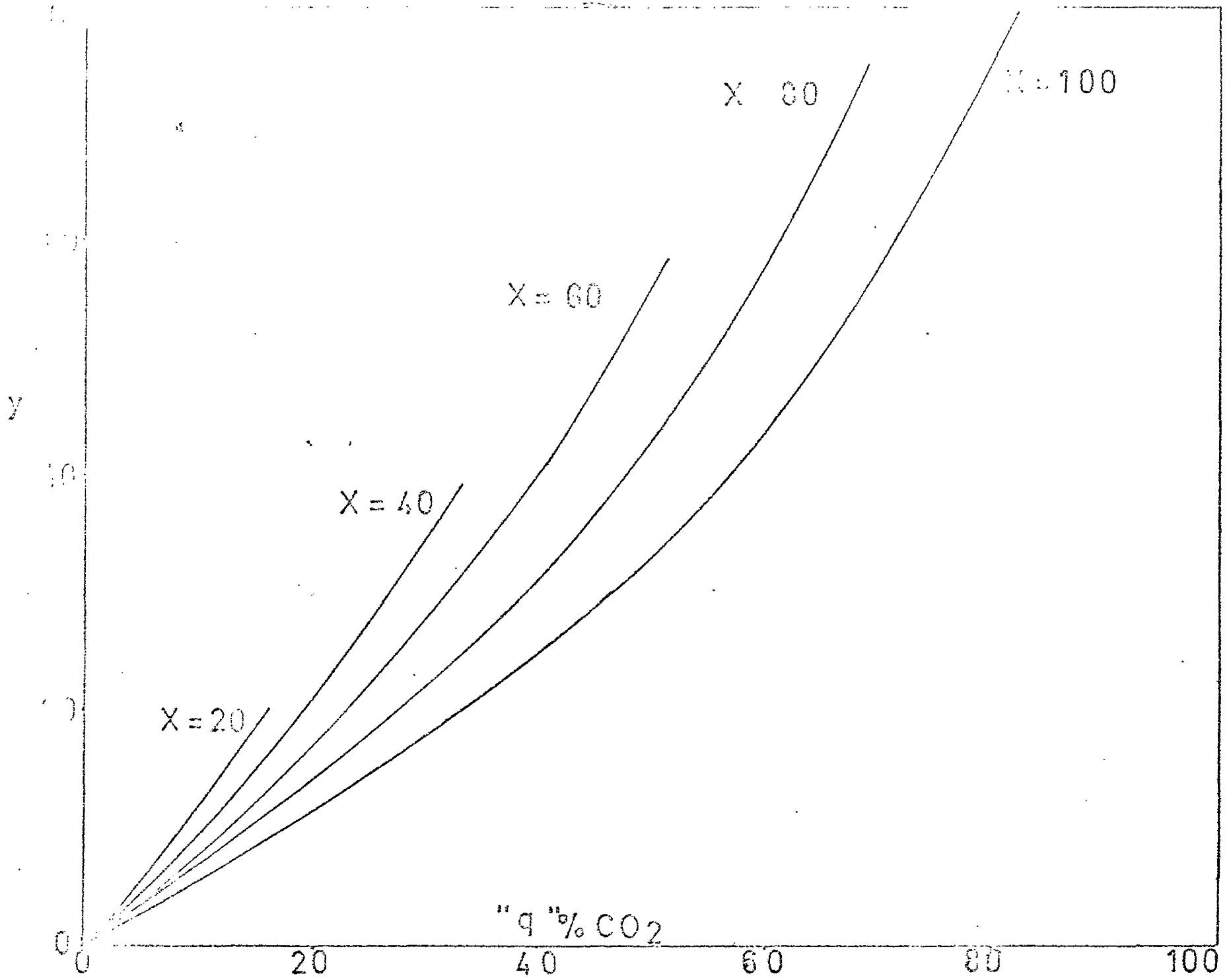
Say inlet gas = 40% CO_2 ; 60% N_2

Direct acting katharometer reads, x = 40

and say differential katharometer reads, q = 5

Then y from Figure 4.9 = 4.3

$\therefore$ Outlet CO_2	= x - y	= 35.7 moles	=	34.2%
CO	= 2y	= 8.6 moles	=	8.3%
N_2	= 100-x	= 60.0 moles	=	57.5%
Total	= 100+y	= 104.3 moles		100.0%



FIG·4·9

4.7. Experimental results.

4.7.1. Attempts to gasify coke carbon. Two attempts were made to gasify powdered high temperature coke at 1200°F and 1300°F in the stainless steel fluidized bed reactor using an inlet gas of 30% carbon dioxide and 70% nitrogen. The particle size range taken for this purpose was -60+100 mesh B.S.S. In neither case was there any indication on the katharometer recorder chart of the formation of a measurable amount of carbon monoxide. This was confirmed by the similarity of the inlet and outlet gas flowrate. No attempt was made to gasify coke at a higher temperature in this reactor.

4.7.2. Reduction of a fluidized-bed of iron ore. The reduction of the powdered iron ore in the stainless steel fluidized bed reactor was carried out by means of hydrogen supplied in high pressure cylinders. The iron ore (particle size range -52+100 mesh B.S.S.) was previously dried for some time at 230°F. A weighed amount was fed into the reactor and the bed fluidized with air while the reactor temperature was raised to a steady value of 1300°F. The air was then gradually replaced by nitrogen from high pressure cylinders. When the air had been suitably displaced, hydrogen was introduced into the reactor together with nitrogen at a total measured flowrate required

to maintain the bed in a suitable state of fluidization. The reduction of the ore was continued until sufficient water had been collected to ensure that the reduction was complete. Complete reduction was confirmed by a check run in which the reactor was opened at the end of the reduction time and the powder from the bed analysed for iron content.

4.7.3. Reaction of carbon dioxide with reduced iron in the fluidized bed. It is well known that reduced iron reacts with carbon dioxide to form iron oxide presumably through the reaction

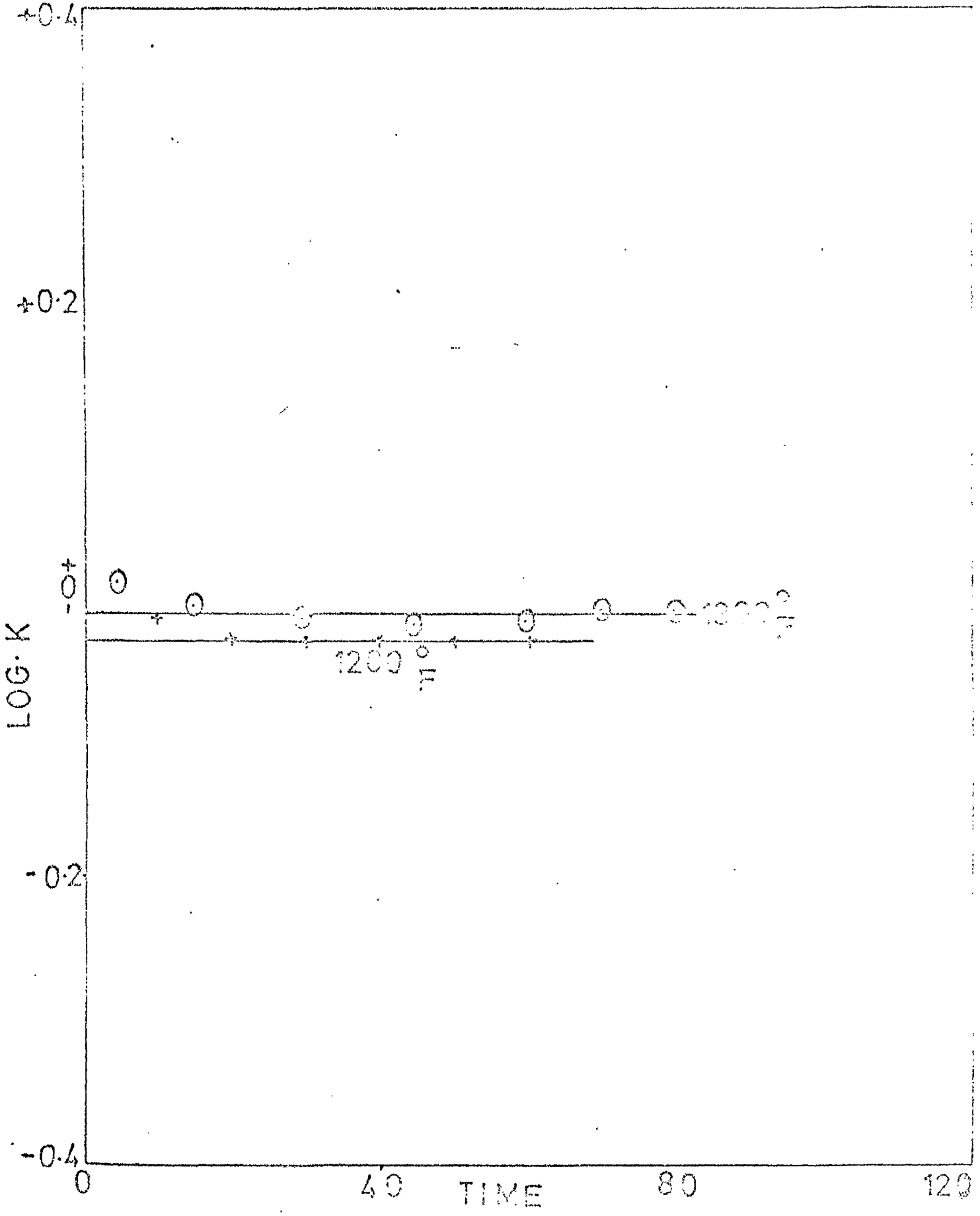
$$Fe + CO_2 = FeO + CO$$

Hence one mole of carbon monoxide is formed for every mole of carbon dioxide in the reaction.

Two experimental runs were undertaken to determine the composition of the exit gas from a bed of freshly reduced iron fluidized with a carbon dioxide; nitrogen mixture at 1200°F and 1300°F. The values obtained were used to calculate equilibrium ratios which were compared with the theoretical equilibrium constant of the reaction between carbon dioxide and iron.

The experimental results are reproduced below in Tables 4.2 and 4.3 and Figure 4.10.

As the reduction and gasification conditions for both cases were identical they are given below before the Tables for results.



FIG·4·10

Reduction conditions

Weight of iron ore bed	=	600 gms.
Particle size range	=	(-52 + 100) mesh B.S.S.
Flowrate of inlet gas	=	0.38 ft^3/min at 20°C.
Composition of inlet gas	=	63% hydrogen and 37% nitrogen.
Temperature of reduction	=	1300°F.
Volume of water collected	=	155 c.c.

Gasification conditions

Flowrate of inlet gas	=	0.303 ft^3/min at 20°C.
Percentage composition of inlet gas	=	30% carbon dioxide and 70% nitrogen.
Inlet and outlet gas temperature	=	21°C.
Pressure under the porous disc	=	25.9 inches of water at 1200°F, and 29.8 inches of water at 1300°F

TABLE 4.2 Equilibrium ratios of carbon dioxide and carbon monoxide over reduced iron at 1200°F.

At (mins)	q %	y	% CO_2	% CO	% N_2	K calculated	Log K calculated
5	10	10	18.2	18.2	63.6	1.00	0.0000
10	7.5	7.0	22.1	13.4	64.5	0.6063	-0.2131
15	6.0	5.3	23.45	10.05	66.5	0.4285	-0.36805
20	6.0	5.3	23.45	10.05	66.5	0.4285	-0.36805

The run was continued for a total of 60 minutes during which there was not further change in the outlet gas composition. The outlet flow rate corrected to the temperature and pressure of the inlet flow was found to be identical with it. This is to be expected from the stoichiometry of the reaction.

TABLE 4.3 Equilibrium ratio of carbon dioxide and monoxide over reduced iron at 1300°F.

At (mins)	q %	y	% CO_2	% CO	% N_2	K	Log K calculated
5	11.0	10.8	17.30	19.50	63.20	1.127	+0.05192
10	9.4	9.00	19.25	16.55	64.20	0.8597	-0.06565
15	8.8	8.20	20.10	15.10	64.80	0.7512	-0.12424
20	8.1	7.80	20.60	14.50	64.90	0.7039	-0.15248
25	7.8	7.10	21.40	13.26	65.34	0.6196	-0.20788
30	7.5	7.00	21.50	13.10	65.40	0.6093	-0.21516
35	7.4	6.90	21.60	12.90	65.50	0.5972	-0.22388
40	7.4	6.90	21.60	12.90	65.50	0.5972	-0.22388
45	7.2	6.60	21.90	12.40	65.70	0.5662	-0.24703
50	7.0	6.50	22.00	12.20	65.80	0.5545	-0.25610
55	7.4	6.90	21.60	12.90	65.50	0.5972	-0.22403
60	7.7	7.05	21.45	13.15	65.40	0.6127	-0.21990
65	7.8	7.10	21.40	13.26	65.44	0.6129	-0.21261
70	8.0	7.50	20.95	13.95	65.10	0.6658	-0.17666
75	8.0	7.50	20.95	13.95	65.10	0.6658	-0.17666
80	8.0	7.50	20.95	13.95	65.10	0.6658	-0.17666

It could be seen from the results that the gas composition was very sensitive to slight changes in reactor temperature to be expected while working at high temperature.

Theoretical calculation of the equilibrium constants of carbon dioxide and carbon monoxide over reduced iron at 1200°F and 1300°F.

The equilibrium constant of a reaction is related to the free energy change by the following relationship

$$\Delta F = - RT_1 \ln K$$

The free energy changes of most of the common reactions are known. The free energy change of a reaction under consideration may be calculated by addition and subtraction of the known values of the free energies of formation of the reactants and products. The calculation of the free energy changes in the reaction of carbon dioxide with iron at 1200°F and 1300°F are shown below :-

		Free energy of formation[92] (ΔF, calories) at	
		1200°F	1300°F
	$C + \frac{1}{2} O_2 = CO$	-46,200	-47,400
	$C + O_2 = CO_2$	-94,575	-94,590
(Subtracting)	$CO_2 = CO + \frac{1}{2}O_2$	+48,375	+47,190
	$Fe + \frac{1}{2}O_2 = FeO$	-48,600	-47,700
	$CO_2 = CO + \frac{1}{2}O_2$	+48,375	+47,190
(Adding)	$Fe + CO_2 = FeO + CO$	- 225	- 510

The required values of free energy may now be inserted into the equation

$$\Delta F = - RT_1 \ln K.$$

The following values of log K were calculated :-

At 1200°F

$$(-225) = (-1.987)\ 922\ (2.303) \log K$$

$$\log K = 0.0531$$

At 1300°F

$$(-510) = (-1.987)\ 977\ (2.303) \log K$$

$$\log K = 0.1140$$

The experimental values for these two temperatures were found to be -0.368 and -0.190 respectively. This may be seen in Figure 4.10. It is evident from these results that in the fluidised bed the reactants had insufficient time of contact to reach equilibrium, but approached quite near to it. The values of off-gas analyses were preserved for comparison with those obtained when carbon dioxide was brought in contact with carbon on iron.

4.7.4. Preliminary attempts to deposit carbon on reduced iron and its removal with carbon dioxide. A number of preliminary experimental runs were carried out with the stainless steel reactor aimed at finding the best reaction conditions for trouble-free running. It was necessary to determine the flowrates of the inlet gases and a suitable inlet gas composition to obtain optimum fluidization in

the bed while the gas expansion due to reaction took place. Owing to the tendency of the particles of freshly reduced iron in the bed to stick together and to the appearance of pyrophoric character, the temperature of the reaction had to be carefully controlled.

The sticking tendency of a reduced iron powder is known to be at a minimum in the temperature range of 1200° - 1400°F but very severe at temperatures above 1400°F.[94] The factors which influence the degree of coherence are

(a) the surface temperature of the particles and the wall temperature of the reactor,

(b) the size of the iron particles, (finer particles have a greater tendency to stick together and to the reactor wall than do particles of larger size),

(c) the extent of reduction (sticking is most severe when the particles of oxide have been metallized to the extent of 20 - 50%), and

(d) the degree or extent of fluidization, (violent fluidization may prevent agglomeration of the bed).

In the preliminary experiments, the iron oxide reduction, carbon deposition and its subsequent removal were all attempted at 1400°F. It was found that to prevent sticking during reduction the inlet flowrate for hydrogen and nitrogen mixture required to be at least 0.38 ft^3/min at

20°C (i.e. superficial linear velocity at 20°C = 0.153 ft/sec) However if such a high flowrate was adhered to, during the carbon deposition, it was found that the carbon deposited on the smallest iron particles caused a lowering of their overall density and these were quickly blown out of the bed. Thus a lower flowrate (0.30 ft^3/min at 20°C = superficial linearvelocity 0.121 ft/sec) was used for the mixture of methane and nitrogen fed during the carbon deposition. A flowrate of the same order was necessary during the carbon removal by carbon dioxide and nitrogen mixture. The optimum temperature range in which carbon could be deposited on iron without sticking troubles making their appearance was found to be 1300 - 1350°F. When the reduction of iron oxide with hydrogen takes place at temperatures at or below 1100°F, the reduced iron particles burn on contact with air. For this reason all reduction runs except when otherwise stated were carried out at 1300°F.

On one occasion when the thermocouple in the bed developed a fault and the bed temperature was in fact in the pyrophoric region without this being apparent from the thermocouple recorder, when the bed was later opened up, a fire resulted. This underlined the importance of accurate bed temperature measurement.

4.7.5. Systematic carbon deposition and subsequent gasification. After overcoming initial difficulties as discussed in the preceding section and selecting the most suitable conditions for operating the unit, systematic studies of the extent of carbon deposition on the iron in the fluidized bed were undertaken and measurements were made of the rate of this carbon gasification by carbon dioxide.

600 gms (1.32 lbs) of iron ore (- 52 + 100 mesh B.S.S.) previously dried at 230°F for 3 hours were charged to the reactor and fluidized with air till a steady bed temperature was obtained. The air was then replaced with nitrogen, and hydrogen later introduced with nitrogen while keeping degree of fluidization constant. After the iron ore particles had been reduced completely, the flow of hydrogen was replaced with nitrogen to maintain the degree of fluidization. Methane from high pressure cylinders was then introduced to the bed together with nitrogen and fluidization continued for a sufficient time to obtain the required amount of carbon on the bed.

The methane used was supplied in cylinders under pressure from a sewage works[95] and was found on analysis to have the composition :-

97.0% methane

3.0% carbon dioxide

While the nitrogen continued to flow into the reactor the flow of methane was stopped at a convenient point and

carbon dioxide from a cylinder introduced to the bed. The gasification of carbon on the bed was followed from the readings on the katharometer recorder, under-bed pressure recorder, and off-gas flowmeters. After gasification had continued for a reasonable time, the carbon dioxide entering the bed was replaced by methane and further carbon deposited on the bed. Deposition and gasification cycles were continued until sufficient information had been obtained.

4.7.6. Principles of carbon deposition calculation. The methane, fed to the reactor for carbon deposition, contained 3% carbon dioxide whose presence initially complicated the calculation of carbon deposition. It was realised that it would have been possible to attempt to remove this carbon dioxide prior to introducing the gas to the reactor, but this was not done due to possible difficulty associated with absorption traps, the back pressure they would develop, and the continued need to check for complete removal of carbon dioxide. It was felt that separation of the carbon dioxide could be made unnecessary by a suitable calculation procedure.

In the reactor due to the presence of the carbon dioxide the following reactions take place,

$$CH_4 \longrightarrow C + 2\,H_2$$

$$CO_2 + C \longrightarrow 2\,CO$$

These reactions cause a dilatation in gas volume so that the N.T.P. flowrate of the gas leaving the reactor is greater than that of the gas entering.

In essence, the "cracking" of methane deposits carbon on the catalyst, and some of this carbon is subsequently removed as carbon monoxide by the carbon dioxide contained in the feed gas. It is required to determine the net deposition of carbon on the catalyst during a run of t minutes.

Basis ..... 100 moles of impure methane

moles of methane fed = 97.0

moles of carbon dioxide fed = 3.0

Let moles of Nitrogen fed = n

and moles of methane decomposed over the catalyst = b

$\therefore$ Moles of methane left = 97 - b

moles of hydrogen formed = 2 b

$\therefore$ Volume of gas leaving reactor after cracking of the methane = 97-b+2b+n = 97+b+n

Thus expansion due to cracking = (97 + b + n)-(100 + n)

= b - 3.0

Percentage decomposition of methane

$$= \frac{100\ b}{97} = 1.03\ b$$

But in the presence of carbon dioxide the reaction

$$CO_2 + C \longrightarrow 2\ CO$$

will take place to some extent.

Thus to a basis of 3.0 moles carbon dioxide fed,

Let moles carbon dioxide reacting with deposited carbon = c

$\therefore$ moles carbon dioxide left = 3 - c

carbon monoxide formed = 2c

$\therefore$ volume of gas leaving reactor after reaction of carbon dioxide = 3 - c + 2c = 3 + c

Thus expansion due to reaction = 3 - c + 2c - 3

= c

Then expansion due to methane decomposition = total measured dilatation-expansion due to carbon monoxide formation, i.e.

b - 3 = D - c

where D is the total dilatation per 100 moles of impure methane

$\therefore$ b = D - c + 3

Now, one mole of methane deposits one atom carbon, and, as well as contributing to the expansion, the production of 2c moles of carbon monoxide results in the removal of c atoms of carbon from the fluidized bed. Thus the net deposition of carbon per 100 moles of impure methane is given by

D - c + 3 - c = D - 2c + 3

Thus if G is the weight of carbon deposited in a run of t minutes,

$$G = \frac{M}{100} (D - 2c + 3)\ 12\ t \qquad lb$$

where M is the number of moles of impure methane fed to the reactor per minute.

Calculation of c. Assume that the reaction of carbon dioxide with deposited carbon in the fluidized bed of catalyst goes to equilibrium at the reaction temperature. The ease with which equilibrium was reached in later experiments suggests that this is a valid assumption.

The reaction

$$CH_4 + CO_2 = 2\,CO + 2H_2$$

is assumed to be covered in this analysis as its effect is really the summation of the deposition of carbon from thermally cracked methane and the reaction of this carbon with carbon dioxide, i.e.

$$CH_4 \longrightarrow C + 2\,H_2$$

$$C + CO_2 \longrightarrow 2\,CO$$

(adding) $$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

The value of c may be obtained from equilibrium data, where the equilibrium constant K is given by the "equation"

$$K = (P_{CO})^2 (P_{CO_2})^{-1}$$

Now $$p_{CO} = \frac{2c}{(97 + b + n) + (3 + c)} = \frac{2c}{100 + b + n + c}$$

and $$p_{CO_2} = \frac{3 - c}{100 + b + n + c}$$

$$K = \frac{4c^2}{(100 + b + n + c)^2} \cdot \frac{(100 + b + n + c)}{3 - c}$$

$$= \frac{4c^2}{(100 + b + n + c)(3 - c)}$$

i.e. $$\frac{4c^2}{K} = (100 + b + n + c)(3 - c)$$

Substituting for $b = D - c + 3$

$$\frac{4c^2}{K} = (100 + D - c + 3 + n + c)(3 - c)$$

$$= (100 + 3 + n)(3 - c)$$

$$\therefore \quad \frac{4c^2}{K} + (103 + D + n)c - (103 + D + n)3 = 0$$

The roots of this quadratic equation are given by

$$c = \frac{-(103+D+n) \pm \left[(103+D+n)^2 + \frac{4(4)3}{K}(100+D+n)\right]^{\frac{1}{2}}}{8/K}$$

Since only the positive root applies here

$$c = \frac{-(103+D+n) + \left[(103+D+n)(103+D+n+\frac{48}{K})\right]^{\frac{1}{2}}}{8/K}$$

Calculation of D.

Let V_1 = inlet flowrate (ft^3/min) impure methane at T_1°C and p_1 inches of water gauge,

V_2 = inlet flowrate (ft^3/min) of N_2 at T_1°C and p_1 inches water gauge,

V_3 = integral outlet flow at T_2°C and atmospheric pressure, assumed to be 406.8 inches water gauge.

$\therefore$ Total inlet moles after t minutes

$$= \frac{(V_1 + V_2)}{359} t \cdot \frac{(273)}{(273 + T)} \cdot \frac{(p_1 + 406.8)}{406.8}$$

Total outlet flow in the same period

$$= \frac{V_3}{359} \cdot \frac{273}{(273 + T_2)} \quad \text{moles.}$$

Assuming that $T_1 = T_2 = T$, i.e. room temperature, then total dilatation over t minutes

$$= \frac{273}{359(273+T)} \left[V_3 - \frac{(V_1 + V_2)\, t\, (p_1 + 406.8)}{406.8} \right]$$

but impure methane passing in t minutes = M t

where $M = \frac{V_1}{359} \cdot \frac{273}{(273+T)} \cdot \frac{(p_1 + 406.8)}{406.8}$

$$\therefore \quad D = \frac{273(100)}{359(273+T)(Mt)} \left[V_3 - \frac{(V_1 + V_2)\, t\, (p_1 + 406.8)}{406.8} \right]$$

Sample calculation.

Run 19:

Carbon deposition temperature	=	1325°F
Flowrate of impure methane, V_1	=	0.16 ft^3/min
" " nitrogen V_2	=	0.14 "
Total quantity of outlet gas	=	15.15 ft^3
Temperature of inlet and outlet gas	=	22°C
Average pressure, p_1	=	44.8 inches of water gauge
Total deposition time	=	40 minutes

Assume that K, at a reaction temperature of 1325°C = 1.4

This value of K is taken from Lavrov's data[44]. It may be argued, perhaps, that this choice of value is unjustified in that chemical equilibrium may not be reached in the reactor. Moreover, as it is shown later that the classical graphite/carbon dioxide equilibrium is "exceeded" by the

reactants in this system, a higher value of K might well have been used. Since, however, the methane only contained a small amount of carbon dioxide, the calculated amount of deposited carbon was not very sensitive to the value of K.

$$M = \frac{0.16}{359} \cdot \frac{(273)}{(295)} \cdot \frac{451.6}{406.8} = 0.000458 \text{ moles/min.}$$

Moles of nitrogen per minute $= \frac{0.14}{359} \cdot \frac{(273)}{(295)} \cdot \frac{451.6}{406.8} = 0.000405$

Thus nitrogen per 100 moles of impure methane

$$n = \frac{0.000405(100)}{0.000458} = 87.4 \text{ moles.}$$

$$D = \frac{273(100)}{359(295)0.000458(40)} \left[15.15 - \frac{0.30(40)\ 451.6}{406.8}\right]$$

$$= 14.05\ [1.85] = 26.0$$

$$c = \frac{-(103+26.0+87.4) + \left[(103+26.0+87.4)\left(103+26.0+87.4+\frac{48}{1.4}\right)\right]^{\frac{1}{2}}}{5.71}$$

$$= \frac{-216.4 + [216.4\ (250.7)]^{\frac{1}{2}}}{5.71} = 2.975$$

% methane decomposition $= 1.031\ (26.0 - 2.975 + 3)$

$= 26.9$

$$G = \frac{0.00458\ (23.05)12(40)}{100} = 0.0507 \text{ lbs.}$$

The weight of carbon deposited in Run 18 (see Table 4.24) was calculated for a range of selected values of K. The values obtained were as follows :-

K	G (lbs)
0.05	0.1003
0.10	0.0978
0.50	0.0933
1.0	0.0925
5.0	0.0917
10.0	0.0914

It may be seen that G becomes increasingly sensitive to K as the value of the letter is reduced. In all later carbon deposition calculations the value of K used was the appropriate average value found for that temperature for the gasification of deposited carbon in our apparatus. The values selected are shown in Table 4.26. A value of K = 8.5 was used for all calculated depositions for carbon at 1325°F.

4.7.7. Comparison of actual carbon deposition with theory. After the carbon deposition had been completed and the reactor cooled to room temperature with nitrogen still fluidising the bed, the reactor was opened and the mixture of reduced iron and deposited carbon were taken out and bottled. The iron content of a representative sample of the mixture was determined by the following procedure :-

A weighed sample (0.279 gms) of the iron-carbon mixture was treated with 30 ml hydrochloric acid (S.G. = 1.16) and the iron dissolved with heat. The residue of carbon and gangue constituents was filtered off and the filtrate diluted to 100 ml with hot water. The solution was boiled while adding dropwise sufficient 20% stannous chloride solution to dispel the yellow coloration. Cold water was then added to bring the total volume to about 200 ml, the solution cooled rapidly to about 30°C and 10 ml of saturated mercuric chloride solution added. When the solution was cooled to room temperature a further 200 ml water was added followed by 50 ml of phosphoric-sulphuric acid mixture (50 ml of syrupy phosphoric acid and 200 ml of concentrated sulphuric acid diluted to 1 litre with water), and a few drops of diphenylamine indicator. This was then titrated with $N/_{20}$ potassium dichromate solution to a bluish-violet end point.

The carbon content of the sample was calculated from a comparison of the iron content of the reduced ore before

deposition of the carbon and that of the final iron-carbon mixture taken from the reactor. It was felt that owing to possible losses of material in opening the reactor, this would give a more accurate estimate of the carbon deposited than a simple measurement of weight increase,

i.e. if W = total weight of material taken from the reactor at the end of the run, and I_1 and I_2 are percentage iron contents of the bed before and after the run, then

$$\text{weight of carbon deposited} = W\left(1 - \frac{I_2}{I_1}\right).$$

Four such experiments were carried out to verify the carbon deposition formula. In Table 4.4 a comparison is made between the weights of carbon calculated from the deposition formula and that given by the weight of material removed from the bed and the ratio of the "before" and "after" iron contents. It may be seen that a good measure of agreement exists between them and that the deposition formula may be used with a certain amount of confidence in spite of the uncertainty of the value of the equilibrium constant for the Boudouard equilibrium.

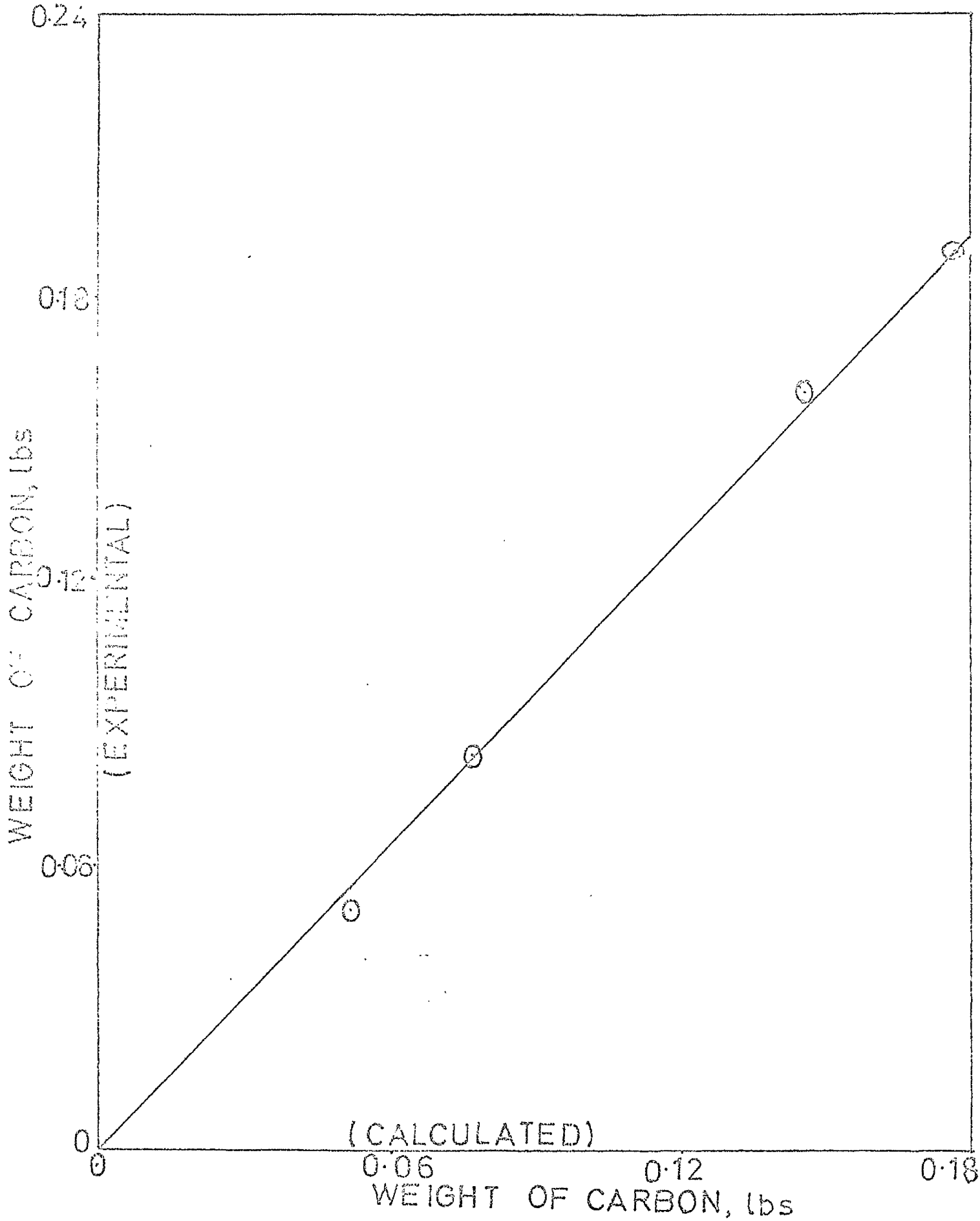
TABLE 4.4

Weight of iron ore before reduction	=	1.32 lbs (600 gm)
Temperature of reaction	=	1325°F
Flowrate of impure methane, V_1	=	0.16 ft^3/min.at 20°C
" " nitrogen, V_2	=	0.14 " "
K at reaction temperature	=	8.5

Run No.	Room Temp. T°C	Duration of expt. (t.mins)	p_1, Average pressure (inches water gauge).	Total outlet flow, (V_3.ft^3)	Carbon deposited (lbs) Calculated	Found
19A	22	40	44.80	15.15	0.0501	0.0485
19B	22	42	57.08	15.45	0.0265	0.0316
19C	24	40	47.72	15.85	0.0691	0.0810
19D	24	40	61.20	15.05	0.0316	0.0313

These results are plotted in Fig. 4.11

4.7.8. Principles of carbon removal calculation. The calculation of the removal of carbon from the bed by the introduction of a mixture of carbon dioxide and nitrogen was based on a carbon balance. In the following discussion x and y have the same significance as earlier and were derived from the katharometer recorder chart.


0·24
0·18
0·12
0·06
0
WEIGHT OF CARBON, lbs
(EXPERIMENTAL)
0
0·06
0·12
0·18
(CALCULATED)
WEIGHT OF CARBON, lbs

FIG·4·11

Let V_4 = inlet flowrate (ft^3/min) of carbon dioxide and nitrogen mixture, at T_1°C and p_2 inches of water gauge.

V_5 = integral outlet flow at T_2°C and atmospheric pressure (assumed to be 406.8 inches of water gauge).

Thus at time t_1 minutes from start of inlet flow V_4, moles of carbon dioxide admitted to the bed

$$= \frac{x}{100} \cdot \frac{(V_4 t_1)}{359} \cdot \frac{273}{273+T_1} \cdot \frac{(p_2 + 406.8)}{406.8}$$

= atoms carbon in.

$$\% (CO_2 + CO) \text{ in outlet gas} = \frac{(x+y)100}{100+y} + \frac{2y(100)}{100+y}$$

$$= \frac{100(x+y)}{100+y} .$$

Total moles of carbon dioxide plus carbon monoxide that have left the bed after t_1 minutes

$$= \left\{\frac{(x+y)}{(100+y)}\right\} \cdot \frac{V_5}{359} \cdot \frac{(273)}{(273+T_2)}$$

= atoms carbon out.

Then total carbon removed from the bed during t_1 minutes

= atoms carbon (out - in) = ΔC

$$= \left\{\frac{(x+y)}{(100+y)}\right\} \cdot \frac{V_5}{359} \cdot \frac{(273)}{(273+T_2)} - \frac{x}{100} \cdot \frac{(V_4 t_1)}{(359)} \cdot \frac{273}{273+T_1} \cdot \frac{(p_2 + 406.8)}{(406.8)}$$

Assuming that $T_1 = T_2 = T$

$$\Delta C = \frac{(273)}{(273+T)} \cdot \frac{1}{359} \cdot \left[\frac{V_5(x+y)}{100+y} - \frac{V_4 t_1 x}{100} \cdot \frac{(p_2 + 406.8)}{406.8} \right]$$

atoms carbon removed from the bed during t_1 minutes of run.

4.7.9. Calculation of oxygen taken up by the bed.

It was realised that, during the admission of a mixture of carbon dioxide and nitrogen to the bed of carbon and iron, it was quite likely that the carbon dioxide would react to some extent with the iron as well as with the carbon. To evaluate the extent to which the iron was oxidized in the presence of the carbon, a formula was derived based on an oxygen balance between inlet and outlet gases. The carbon dioxide content of the methane which came in contact with iron during the deposition of carbon might have a slight effect on the results, but from a consideration of the facts, it was decided to neglect it.

The bed during the passage of carbon dioxide should absorb oxygen by the reaction

$$Fe + CO_2 = CO + FeO$$

or other similar reaction. During the passage of carbon dioxide,

moles of oxygen admitted = atoms of carbon admitted;

and moles of oxygen leaving the bed = moles of carbon dioxide out + ½ moles of carbon monoxide out.

$$\% CO_2 + \tfrac{1}{2}\% CO = \frac{(x - y)100}{(100+y)} + \frac{100\ y}{100+y} = \frac{100\ x}{100+y}.$$

Then if ΔO = atoms of oxygen absorbed by the bed in t_1 minutes.

$$\therefore \Delta O = \frac{2x}{100} \cdot \frac{(V_4 t_1)}{(359)} \cdot \frac{273}{273+T} \cdot \frac{(p_2+406.8)}{406.8} - \frac{2x}{100+y} \cdot \frac{V_5}{(359)} \cdot \frac{273}{(273+T)}$$

$$= \frac{273}{(273+T)} \cdot \frac{2x}{359} \left[\frac{V_4 t_1}{100} \cdot \frac{(p_2 + 406.8)}{406.8} - \frac{V_5}{100+y} \right]$$

4.7.10 Gasification runs and results obtained.

With the fluid-bed gasification apparatus and the associated recording analytical instruments, it was relatively easy to carry out a large number of experimental gasification runs in a relatively short time and to obtain thereby a considerable quantity of data. A number of these runs have been selected for presentation here and the experimental conditions under which they were carried out are listed in Table 4.5.

Runs 16 to 20 were carried out at four different gasification temperatures. During each run at a particular temperature, the carbon deposition and gasification cycle was repeated several times to determine the trend in the Boudouard equilibrium ratio with gasification time (i.e. amount of carbon on the bed) and with life of catalyst (i.e. age and oxygen content of iron in bed).

Run 22 was carried out to study the effect of partial pressure of carbon dioxide on the equilibrium ratio and on the rate of gasification of carbon.

In Run 23 the effect of reducing the iron with hydrogen at a temperature which confers pyrophoric character on the reduced iron was considered.

In Run 33 air was used in place of carbon dioxide.

In all the experiments, the amount of iron ore put in the reactor was 1.32 lbs (600 gms).

The experimental data for Run 16 in which ten deposition:gasification cycles were carried out is given

TABLE 4.5

Run No.	No. of repetition	Carbon deposition Temp. °F	Carbon deposition inlet flowrate, $ft^3/min.$ N_2	Carbon deposition inlet flowrate, $ft^3/min.$ CH_4	Carbon gasification Temp. °F	Carbon gasification Inlet flowrate, $ft^3/min.$ (total)	Carbon gasification Inlet gas composition % N_2	% CO_2	% O_2
16	10 (B-K)	1325	0.14	0.16	1200	0.254	70	30	
17	8 (A-H)	1325	0.14	0.16	1100	0.289	70	30	
18	1	1325	0.14	0.16	1000	0.340	70	30	
20	4 (A-D)	1325	0.14	0.16	1300	0.303	70	30	
22	5 (A-E)								
	A	1325	0.14	0.16	1100	0.291	60	40	
	B	1325	0.14	0.16	"	0.290	50	50	
	C	1325	0.0	0.30	"	0.290	80	20	
	D	1325	carbon carried over from C		"	0.288	90	10	
	E	1325	0.0	0.30	"	0.333	70	30	
23	6 (A-F)								
	A	1100	0.0	0.30	1100	0.274	70	30	
	B	1100	0.0	0.30	"	0.274	70	30	
	C	1200	0.0	0.30	1200	0.254	70	30	
	D	1200	0.0	0.30	1000	0.340	70	30	
	E	1325	0.14	0.16	1300	0.303	70	30	
	F	1200	0.0	0.30	1100	0.274	70	30	
33	1	1325	0.14	0.16	1100	0.255	79	-	

in detail below in Tables 4.6 - 4.15.

It may be seen that for each gasification run the value "q"% carbon dioxide, the reading of the differential katharometer, has been tabulated at five minute intervals together with the total exit gas volume up to each instant of measurement.

As explained earlier, the exit-gas analysis may be determined from x% carbon dioxide in the inlet gas and "q" % in the outlet gas by the use of curves, Figure 4.8 and Figure 4.9. In order to handle quickly and more accurately the large amount of data coming from the gasification unit, it was decided to evaluate the exit-gas analysis, and, from this, the equilibrium ratio by means of a Ferranti Sirius computor. At the same time the computor was asked to calculate the progressive removal of carbon from the bed by means of the carbon balance technique described above, and also the uptake of oxygen by the iron through the oxygen balance. The data provided for the scale shape curve (Figure 4.8) enabled a cubic equation to be set up of the form

$$Z = \alpha(x - q) + \beta(x^2 - q^2) + \delta(x^3 - q^3)$$

and the constants α, β and δ were evaluated by a least-squares procedure.

The relation between x, y and Z may be written in the form

$$\frac{100(x-y)}{(100+y)} + \frac{200\ y(11.3 + 0.06x + 0.053y)}{(100+y)^2} - Z = 0$$

It was decided to solve for y by an iterative method. The iterative equation adopted was that discussed by Lapidus[96] and in principle is used as follows :

Let F(y) be the value of the left hand side of the equation above, when a trial value of y is substituted. Successive values of y are determined from

$$y_{n+1} = \frac{y_{n-1} F(y_n) - y_n F(y_{n-1})}{F(y_n) - F(y_{n-1})}$$

A Sirius Autocode programme was prepared in which

(i) Z was evaluated from the cubic equation in x and q, using the constants α, β and δ.

(ii) two trial values of y (i.e. y_0, y_1) were specified and the computer was instructed to solve for y_2 and subsequent values of y until two successive values agreed to five significant figures. The last value of y was rounded off and taken as the value which satisfied the equation.

The computer was asked to tabulate for each gasification run the following, under the headings shown below :

Time in run (t_1 mins.)	"Time"
Percentage of inlet carbon dioxide decomposed (y)	"Y"
Percentage carbon dioxide in outlet gas...	"CO_2"
Percentage carbon monoxide in outlet gas..	"CO"
Boudouard equilibrium ratio	"K"
Weight of carbon deposited in time interval (gm.)	"C_1"
Total weight of carbon deposited up to the end of the total stated time.	"C_2"

Weight of oxygen absorbed by the bed in time interval (gm) ..... "O_1"

Total weight of oxygen absorbed up to the end of total stated time ..... "O_2"

The weight unit of the gramme was preferred here to that of the pound due to the small amount of material involved and the greater convenience that this gave in the computor print-out.

Thus $C_1 = \Delta C\ (12)\ 453.6$

and $O_1 = \Delta O\ (16)\ 453.6$

The computor print-out sheets for Runs 16B to 16K are paged in front of each appropriate table of experimental data,

From the computed results for carbon deposition and removal at each stage in the run, it was possible to calculate the approximate carbon content of the bed at the end of the run, and to compare this with the value obtained by direct chemical analysis of the bed. In such cases where the bed contained not only iron, carbon and gangue constituents, but also oxidised material, the chemical analysis involved solution of the iron in acid and its subsequent determination as described in page 102, together with the weighing of the undissolved residue (containing carbon and gangue) and the calculation of the carbon content from the known gangue content. It was found in all cases that good agreement was

obtained between calculated and determined carbon content of the bed. This is illustrated by the figures given below for Run 23.

Calculated total weight of carbon deposited	=	0.6882 lb
" " " gasified	=	0.3189 lb
" weight of carbon on bed at end of run	=	0.3693 lb

Weight of bed at end of run = 0.736 lb

Composition of bed :-

Fe	= 67.65%
C	= 15.55%
Gangue	= 4.85%
Oxygen	= 11.95%
	100.00% by weight

∴ Weight of carbon on bed = 0.1117 lb

Weight of solids in cyclone at end of run = 0.442 lb

Composition of cyclone solids:-

Fe	= 43.85%
C	= 53.05%
Gangue	= 3.15%
Oxygen	= Nil
	100.00% by weight

∴ Weight of carbon in cyclone solids 0.2345

∴ Total weight of carbon found 0.3462

For Run 17, only the carbon deposition results and the computer print-out sheets for the gasification parts of each cycle are given in Tables 4.16 to 4.23. For the remaining runs (except for Run 33) whose reaction conditions are given in Table 4.5, in order to reduce the bulk of this work only the results derived from the computer sheets are included in Tables 4.24. Run 33 results are tabulated in Table 4.25.

RUN 16 (B - K)

The material in the reactor at the start of the carbon deposition part of the cycle for 16B was reduced iron which had been through a number of deposition and gasification cycles in a previous unreported run.

(For all the other runs reported, the material in in the bed at the start of the first carbon deposition was freshly reduced iron ore).

The following variables were held constant during this series of cycles :-

DEPOSITION OF CARBON

Composition of the inlet gas :-

Methane (V_1) = 0.16 ft^3/min.

Nitrogen (V_2) = 0.14 ft^3/min.

Reaction temperature = 1325°F

CARBON REMOVAL

Gasification mixture = 30% carbon dioxide and 70% nitrogen.

Total inlet flowrate of gasification mixture (V_4) = 0.254 ft^3/min.

Reaction temperature = 1200°F

The other reaction variables which differed from experiment to experiment are given under the appropriate heading.

TIME	V	CO_2	CO
5	17.77	10.37	30.19
10	17.77	10.37	30.19
15	17.20	10.92	29.35
20	17.20	10.92	29.35
25	17.20	10.92	29.35
30	17.77	10.37	30.19
35	17.77	10.37	30.19
40	17.77	10.37	30.19
45	17.77	10.37	30.19
50	18.07	9.82	31.04
55	17.73	10.37	30.19
60	17.20	10.92	29.35
65	17.20	10.92	29.35
70	17.20	10.92	29.35

TABLE 4.6 RUN 16B

CARBON DEPOSITION

Total outlet gas flow (V_3) = 39.2 ft^3

Room temperature (T) = 20°C

Total reaction time (t) = 100 minutes

Average pressure of inlet gas (p_1) = 48.48 inches of water gauge

Average decomposition of methane = 32.4%

Calculated weight of carbon deposited in t minutes (G) = 0.1588 lb

Average rate of carbon deposition (G/t) = 1.588×10^{-3} lb /min

CARBON REMOVAL

Total gasification time (t_1) = 70 minutes

Average pressure for inlet gas (p_2) = 50.08 inches of water gauge

t_1 (mins)	q %	V_5 ft^3
5	15.0	1.3
10	15.0	2.9
15	14.5	4.5
20	14.5	6.05
25	14.5	7.60
30	15.0	9.16
35	15.0	10.73
40	15.0	12.30
45	15.0	13.80
50	15.5	15.30
55	15.0	16.9
60	14.5	18.5
65	14.5	20.0
70	14.5	21.5

Weight of carbon removed = 0.084 lb

Rate of carbon removal = 1.20×10^{-3} lb/min

Weight of oxygen absorbed = 0.0417 lb

Rate of oxygen absorption = 0.595×10^{-3} lb/min

TABLE 4.7 RUN 16C

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	12.6 ft^3
Room temperature (T)	=	20°C
Total reaction time (t)	=	30 minutes
Average pressure of inlet gas (p_1)	=	51.2 inches of water gauge
Average decomposition of methane	=	47.1%
Calculated weight of carbon deposited in t minutes (G)	=	0.0719 lb
Average rate of carbon deposition (G/t)	=	2.396×10^{-3} lb /min

CARBON REMOVAL

Total gasification time (t_1)	=	70 minutes
Average inlet gas pressure (p_2)	=	50.8 inches of water gauge

t_1 (mins)	q %	V_5 ft^3
5	15.0	1.65
10	15.0	3.15
15	15.0	4.65
20	15.0	6.22
25	15.0	7.80
30	15.0	9.27
35	15.0	10.75
40	15.0	12.34
45	15.0	13.94
50	15.0	15.44
55	15.0	16.95
60	15.0	18.54
65	15.0	20.14
70	15.0	21.60

Weight of carbon removed	=	0.0860 lb
Rate of carbon removal	=	1.229×10^{-3} lb /min
Weight of oxygen absorbed	=	0.0413 lb
Rate of oxygen absorption	=	0.590×10^{-3} lb/min

TIME	Y	CO_2	CO
5	17.73	10.37	30.
10	17.73	10.37	30.
15	17.73	10.37	30.
20	17.73	10.37	30.
25	17.73	10.37	30.
30	17.73	10.37	30.
35	17.73	10.37	30.
40	17.73	10.37	30.
45	17.73	10.37	30.
50	17.73	10.37	30.
55	17.73	10.37	30.
60	17.72	10.37	30.
65	17.72	10.37	30.
70	17.72	10.37	30.

RUN 16D

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
5	10.57	0.72	32.73	1.228	3.201	3.29	2.175	2.17
10	18.07	0.27	31.89	1.006	2.033	6.22	2.070	5.14
15	18.07	0.27	31.89	1.006	2.033	9.16	2.070	8.11
20	18.07	0.32	31.04	0.981	2.868	12.03	2.022	10.94
25	17.78	10.37	30.10	0.879	2.804	14.83	2.674	13.61
30	17.73	10.37	30.10	0.879	2.018	17.75	2.001	15.90
35	17.55	10.50	30.86	0.841	2.940	20.70	2.030	17.94
40	17.31	10.81	30.52	0.806	2.006	23.00	4.005	20.04
45	17.20	10.22	30.35	0.789	2.040	25.33	3.374	23.27
50	17.31	10.81	30.52	0.806	2.006	28.20	2.171	25.80
55	17.31	10.81	30.52	0.806	2.003	31.12	1.079	30.06

Average rate of carbon deposition = 2.045×10^{-3} lb / min.

CARBON REMOVAL

Total gasification time (t_1) = 55 minutes

Average inlet gas pressure (p_2) = 52.7 inches of water gauge

t_1 (mins)	q %	V_5 ft^3
5	16.5	1.60
10	16.0	3.15
15	16.0	4.70
20	15.5	6.25
25	15.0	7.80
30	15.0	9.37
35	14.8	10.95
40	14.6	12.42
45	14.5	13.90
50	14.6	15.47
55	14.6	17.05

Weight of carbon removed = 0.0686 lb
Rate of carbon removal = 1.247 lb/min
Weight of oxygen absorbed = 0.0331 lb
Rate of oxygen absorption = 0.602 lb/min

TABLE 4.9 RUN 16E

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	17.95 ft_3
Room temperature (T)	=	21°C
Total reaction time (t)	=	45 mins
Average pressure of inlet gas(p_1)	=	49.45 ins.water gauge
Average decomposition of methane	=	35.9%
Calculated weight of carbon deposited in t minutes (G)	=	0.0798 lb
Average rate of carbon deposition ($G/_t$)	=	1.774×10^{-3} lb/min

CARBON REMOVAL

Total gasification time (t_1)	=	80 mins.
Average inlet gas pressure (p_2)	=	51.5 ins.water gauge

t_1 (min.)	q %	V_5 ft^3
5	16.5	1.65
10	16.0	3.16
[illegible]	[illegible]	[illegible]

RUN 16E

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
5	[illegible]	9.72	32.73	1.228	3.600	3.60	1.147	1.15
10	[illegible]	9.27	31.89	1.096	2.717	6.32	3.644	4.72
[illegible]	[illegible]	10.37	30.19	0.879	2.548	8.96	3.165	7.23
[illegible]	[illegible]	10.37	30.19	0.879	2.705	11.67	2.973	10.03
[illegible]	[illegible]	10.37	30.19	0.879	2.705	14.37	2.973	13.00
[illegible]	[illegible]	10.37	30.19	0.879	2.648	17.02	3.165	16.17
[illegible]	[illegible]	10.37	30.19	0.879	2.648	19.67	3.165	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	3.106	22.77	1.632	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	3.221	26.00	1.649	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.819	28.81	2.590	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.819	31.63	2.590	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.533	34.17	3.548	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.533	36.70	3.548	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.877	39.58	2.398	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.934	42.51	2.207	[illegible]
[illegible]	[illegible]	10.37	30.19	0.879	2.934	45.44	2.207	[illegible]

TABLE 4.10 RUN 16F

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	20.4 ft^3
Room temperature (T)	=	21°C
Total reaction time (t)	=	50 mins
Average pressure of inlet gas (p_1)	=	52.4 ins.water gaug
Average decomposition of methane	=	35%
Calculated weight of carbon deposited in t min.(G)	=	0.0994 lb
Average rate of carbon deposition ($G/_t$)	=	1.989×10^{-3} lb/min

CARBON REMOVAL

Total gasification time (t_1)	=	75 min
Average pressure of inlet gas (p_2)	=	52.3 ins.water gaug

t_1 (mins)	q %	V_5 ft^3
5	16.5	1.60
10	15.0	3.09
15	14.8	4.58
20	15.0	6.14
25	15.0	7.70
30	15.0	9.25
35	15.0	10.80
40	15.0	12.34
45	14.8	13.88
50	14.5	15.44
55	14.5	17.00
60	14.5	18.51
65	14.5	20.02
70	14.5	21.61
75	14.5	23.20

Weight of carbon removed	=	0.09140 lb
Rate of carbon removal	=	1.218×10^{-3} lb/min
Weight of oxygen absorbed	=	0.0440 lb
Rate of oxygen absorption	=	0.587×10^{-3} lb/min

TIME	Y	CO_2	CO
5	19.57	3.72	32.7
10	17.78	10.37	30.1
15	17.55	10.59	29.8
20	17.73	10.37	30.1
25	17.78	10.[illegible]	30.1
30	17.78	10.37	30.1
35	17.78	10.37	30.1
40	17.78	10.37	30.1
45	17.55	10.59	29.8
50	17.20	10.92	29.3
55	17.20	10.92	29.3
60	17.20	10.92	29.3
65	17.20	10.92	29.3
70	17.20	10.92	29.3
75	17.20	10.92	29.3

TABLE 4.11 RUN 16G

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	20.4 ft^3
Room temperature (T)	=	21°C
Total reaction time (t)	=	50 mins
Average pressure of inlet gas (p_1)	=	52.32 ins. of water ga
Average decomposition of methane	=	39.4%
Calculated weight of carbon deposited in t mins (G)	=	0.0803 lb
Average rate of carbon deposition ($G/_t$)	=	1.607×10^{-3} lb/min

CARBON REMOVAL

Total gasification time (t_1)	=	55 mins
Average pressure of inlet gas (p_2)	=	52.15 ins. water gauge

t_1 (mins)	q %	V_5 ft^3
5	15.0	1.58
10	15.0	3.12
15	15.0	4.66
20	15.0	6.21
25	15.0	7.75
30	15.0	9.28
35	15.0	10.82
40	15.0	12.83
45	15.0	14.02
50	15.0	15.54
55	15.0	17.08

RUN 16G

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
5	17.78	10.37	30.19	0.879	2.973	2.97	3.054	2.05
10	17.78	10.37	30.19	0.879	2.744	5.72	2.818	4.37
15	17.78	10.37	30.19	0.879	2.744	8.46	2.818	7.69
20	17.78	10.37	30.19	0.879	2.801	11.26	2.627	10.32
25	17.78	10.37	30.19	0.879	2.744	14.01	2.818	13.13
30	17.78	10.37	30.19	0.879	2.687	16.69	3.008	15.14
35	17.78	10.37	30.19	0.879	2.744	19.44	2.818	18.00
40	17.78	10.37	30.19	0.879	3.144	22.58	1.493	20.44
45	17.78	10.37	30.19	0.879	3.030	25.61	1.863	22.50
50	17.78	10.37	30.19	0.879	2.630	28.24	3.199	25.50
55	17.78	10.37	30.19	0.879	2.516	30.76	3.531	29.00

TABLE 4.12 RUN 16H

CARBON DEPOSITION

RUN 16H

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
0	1.037	9.37	31.39	1.0656	2.705	2.70	3.587	0.00
5	1.079	10.37	30.19	0.879	2.573	5.28	3.301	1.39
10	1.079	10.37	30.19	0.879	2.573	7.96	3.301	10.12
15	1.079	10.37	30.19	0.879	2.573	10.56	3.301	15.11
20	1.079	10.37	30.19	0.879	2.573	13.31	3.726	17.00
25	1.079	10.37	30.19	0.879	3.000	16.35	1.769	17.18
30	1.079	10.37	30.19	0.879	3.000	19.44	1.577	17.51
35	1.079	10.37	30.19	0.879	3.000	22.25	3.535	22.71
40	1.079	10.37	30.19	0.879	3.003	25.06	3.535	24.83
45	1.078	10.37	30.19	0.879	3.210	28.27	1.194	25.44
50	1.037	9.32	31.04	0.981	3.277	31.54	1.349	26.79
55	1.037	9.32	31.04	0.981	3.700	34.24	3.254	30.04
65	1.037	9.32	31.04	0.981	3.757	37.00	3.063	33.11

5	16.0	1.50
10	15.0	3.00
15	15.0	4.50
20	15.0	6.02
25	15.0	7.55
30	15.0	9.13
35	15.0	10.72
40	15.0	12.26
45	15.0	13.80
50	15.0	15.41
55	15.5	17.02
60	15.5	18.53
65	15.5	20.05

Weight of carbon removed = 0.0815 lb

Rate of carbon removal = 1.254×10^{-3} lb/min

Weight of oxygen absorbed = 0.0364 lb

Rate of oxygen absorption = 0.561×10^{-3} lb/min

TABLE 4.13 RUN 16I

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	26.16 ft^3
Room temperature (T)	=	21°C
Total reaction time (t)	=	70 mins
Average inlet gas pressure (p_1)	=	46.7 ins.water gauge
Average decomposition of methane	=	29.3%
Calculated weight of carbon deposited in t mins.(G)	=	0.074 lb
Average rate of carbon deposition ($G/_t$)	=	1.057×10^{-3} lb/min

CARBON REMOVAL

Total gasification time (t_1)	=	65 mins
Average inlet gas pressure (p_2)	=	50.4 ins.water gauge

t_1 (mins)	q %	V_5 ft^3
5	16.0	1.50
10	15.0	3.05
15	14.5	4.60
20	14.5	6.12
25	14.5	7.65
30	14.5	9.17
35	15.0	10.70
40	15.0	12.29
45	15.0	13.88
50	15.0	15.36

RUN 16I

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 4.14 RUN 16J

CARBON DEPOSITION

RUN 16J

TIME	Y	CO_2	CO	K	C_1	C_2	C_3	C_4
5	1.010	0.117	32.000	1.372	0.340	0.034	2.334	0.00
10	1.007	0.087	32.00	1.003	2.017	0.00	2.000	0.00
15	1.007	0.087	32.00	1.003	2.017	0.017	2.000	0.00
20	1.007	0.087	32.00	1.003	2.017	10.00	2.000	11.04
25	1.007	0.087	32.00	1.003	3.206	12.00	2.000	12.00
30	1.007	0.087	32.00	1.003	3.206	12.00	2.000	12.00
35	1.007	0.087	32.00	1.003	2.305	10.00	4.000	20.12
40	1.007	0.087	32.00	1.003	2.453	22.00	4.507	24.04
45	1.010	12.059	26.81	0.571	5.001	20.00	-7.000	17.00

t_1 (mins)	q %	V_5 ft^3
5	17.0	1.60
10	16.0	3.15
15	16.0	4.70
20	16.0	6.25
25	16.0	7.85
30	16.0	9.45
35	16.0	10.91
40	16.0	12.38
45	13.0	14.43

Weight of carbon removed = 0.0631 lb
Rate of carbon removal = 1.403×10^{-3} lb/min
Weight of oxygen absorbed = 0.0187 lb
Rate of oxygen absorption = 0.414×10^{-3} lb/min

TABLE 4.15 RUN 16K

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	19.05 ft^3
Room temperature (T)	=	21°C
Total reaction time (t)	=	50 mins
Average inlet gas pressure (p_1)	=	53.6 ins.water gauge
Average decomposition of methane	=	23.6%
Calculated weight of carbon deposited in t mins.(G)	=	0.0561 lb
Average rate of decomposition ($G/_t$)	=	1.123×10^{-3} lb/min

CARBON REMOVAL

Total gasification time (t_1)	=	45 mins
Average inlet gas pressure (p_2)	=	55.8 ins.water gauge

t_1 (mins)	q %	V_5 ft^3
5	17.5	1.550
10	17.0	3.175
15	16.5	4.800
20	16.0	6.300
25	[illegible]	[illegible]

RUN 16K

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
5	20.72	7.55	34.44	1.554	3.076	3.01	3.620	3.62
10	20.[illegible]	8.[illegible]7	33.58	1.579	3.452	3.53	3.069	5.[illegible]
15	19.[illegible]	[illegible].78	32.73	1.533	3.385	3.91	2.915	7.[illegible]
20	18.[illegible]	9.[illegible]7	31.89	1.096	2.503	12.51	2.183	11.[illegible]
25	17.[illegible]	10.[illegible]	30.35	0.788	2.405	14.01	3.[illegible]	15.42
30	16.[illegible]	11.[illegible]	28.50	0.708	2.524	17.53	3.[illegible]	18.01
35	15.[illegible]	12.[illegible]	26.81	0.571	2.404	20.05	2.[illegible]	20.[illegible]
40	13.[illegible]	14.[illegible]	25.42	0.375	1.429	21.46	4.[illegible]	24.[illegible]
45	11.55	15.[illegible]	24.36	0.247	1.218	22.68	4.[illegible]	25.[illegible]

RUN 17 (A - H)

The following reaction variables were held constant throughout this run.

CARBON DEPOSITION

Inlet gas composition :-

Methane (V_1)	=	0.16 ft^3/min
Nitrogen (V_2)	=	0.14 ft^3/min
Reaction temperature	=	1325°F

CARBON REMOVAL

Gasification mixture	=	30% carbon dioxide and 70%nitrogen
Total inlet flowrate of Gasification mixture (V_4)	=	0.289 ft^3/min
Reaction temperature	=	1100°F

The other reaction variables which differed from experiment to experiment are given under the appropriate heading.

TABLE 4.16 RUN 17A

CARBON DEPOSITION

RUN 17A

TIME	Y	CO_2	CO	X	C_1	C_2	O_1	O_2
5	11.12	12.99	20.03	0.235	2.823	2.82	-1.159	-1.16
10	10.03	12.99	18.32	0.195	1.148	3.97	1.733	0.57
15	10.39	17.76	18.83	0.200	1.697	5.67	0.759	1.33
20	10.19	17.99	18.49	0.190	2.695	8.36	-1.305	0.0
25	10.09	12.99	18.32	0.195	2.170	10.53	-0.323	-0.22
30	10.03	12.99	18.32	0.195	2.170	12.70	-0.303	-0.52
35	10.09	12.99	18.32	0.195	2.170	14.87	-0.303	-0.83
40	10.09	12.99	18.32	0.195	1.659	16.53	0.715	-0.17
45	10.09	12.99	18.32	0.195	2.170	18.70	-0.303	-0.47
50	10.09	12.99	18.32	0.195	2.170	20.87	-0.303	-0.77

CARBON REMOVAL

Total gasification time (t_1)	=	50 mins
Average pressure of inlet gas (p_2)	=	50.1 ins.water gauge
Total outlet flow of gas (V_5)	=	15.8 ft^3
Weight of carbon removed	=	0.046 lb
Rate of carbon removal	=	0.920 x 10^{-3} lb/min
Weight of oxygen absorbed	=	0 lb
Rate of oxygen absorption	=	0 lb/min

TABLE 4.17 RUN 17B

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	22.4 ft^3
Room temperature (T)	=	22°C
Total reaction time (t)	=	60 mins
Average pressure of inlet gas (p_1)	=	51.0 ins.water gauge
Average decomposition of methane	=	20.5%
Calculated weight of carbon deposited in t mins(G)	=	0.0565 lb
Average rate of carbon deposition (G/t)	=	0.941 x 10^{-3} lb/min

RUN 17B

TIME	Y	CO_2	CO	K	C_1	O_2	O_1	O_2
5	18.03	18.09	18.32	0.185	1.366	1.37	1.325	1.33
10	17.97	18.07	17.13	0.155	2.038	3.40	-0.308	1.02
15	17.93	18.09	16.96	0.152	2.025	5.43	-0.324	0.69
20	17.91	18.07	17.13	0.155	2.021	7.72	-0.321	-0.13
25	17.87	18.06	17.30	0.160	1.346	9.27	0.730	0.56
30	17.87	18.06	17.30	0.160	1.709	11.06	0.219	0.32
35	17.87	18.06	17.30	0.160	2.052	13.12	-0.293	0.55
40	17.91	18.05	17.47	0.164	2.319	15.44	-0.799	-0.23
45	17.93	18.03	17.98	0.176	3.378	18.81	-2.782	-3.04
50	17.93	18.03	17.98	0.176	0.578	19.39	2.827	-0.11
55	17.95	18.04	17.64	0.168	2.332	21.72	-0.773	-0.22
60	17.91	18.05	17.47	0.164	1.558	23.28	0.743	-0.24
65	17.91	18.05	17.47	0.164	2.167	25.45	-0.792	-0.76
70	17.95	18.04	17.64	0.168	2.536	28.03	-1.804	-2.02
75	18.01	18.09	18.32	0.193	1.110	29.14	1.934	-0.13
80	18.01	17.99	18.49	0.198	2.043	31.19	0.017	-0.13
85	18.01	17.99	18.49	0.198	1.890	33.08	0.323	0.13
90	18.01	17.99	18.49	0.198	1.890	34.97	0.323	0.49
95	18.01	17.99	18.49	0.198	2.145	37.11	-0.186	0.30
100	18.01	17.97	18.66	0.195	1.546	38.76	0.845	1.17
105	18.03	17.97	18.66	0.195	2.159	40.92	-0.171	0.97
110	18.03	17.97	18.66	0.195	2.261	43.18	-0.374	0.56
115	18.03	18.09	18.32	0.185	2.541	45.72	-1.016	-0.42
120	18.03	18.09	18.32	0.185	1.366	47.08	1.325	0.91

TABLE 4.18 RUN 17C

CARBON DEPOSITION

RUN 17C

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
5	0.56	19.75	15.76	0.136	1.520	1.53	0.404	0.40
10	0.76	19.53	16.11	0.133	1.355	2.89	0.845	1.25
15	0.86	19.30	16.52	0.144	1.503	4.48	0.476	1.73
20	0.47	18.76	17.30	0.160	2.150	6.63	-0.489	1.24
25	0.89	18.31	17.08	0.176	2.306	8.93	-0.631	0.81
30	0.67	18.54	17.64	0.168	2.177	11.11	-0.458	0.15
35	0.57	18.65	17.47	0.164	1.200	12.31	1.469	1.62
40	0.47	18.76	17.30	0.160	1.307	14.31	0.023	1.64
45	0.47	18.76	17.30	0.160	2.040	16.26	-0.234	1.35
50	0.47	18.76	17.30	0.160	2.301	18.56	-0.756	0.56
55	0.47	18.76	17.30	0.160	1.501	20.05	1.046	1.60
60	0.47	18.76	17.30	0.160	1.543	21.40	0.739	2.34
65	0.37	18.87	17.13	0.155	1.385	23.17	-0.197	2.15
70	0.37	18.87	17.13	0.155	1.187	25.26	-0.607	1.54
75	0.37	18.87	17.13	0.155	1.034	27.60	-0.095	1.44
80	0.37	18.87	17.13	0.155	1.430	29.02	0.930	2.37

Average pressure of inlet gas (p_2) = 53.25 ins.water gauge

Total outlet gas flow (V_5) = 24.90 ft^3

Weight of carbon removed = 0.0639 lb

Rate of carbon removal = 0.798 x 10^{-3} lb/min

Weight of oxygen absorbed = 0.0052 lb

Rate of oxygen absorption = 0.065 x 10^{-3} lb/min

TABLE 4.19 RUN 17D

CARBON DEPOSITION

Total outlet gas flow (V_3)	=	7.92 ft^3
Room temperature (T)	=	22°C
Total reaction time (t)	=	20 mins
Average pressure of inlet gas (p_1)	=	52.4 ins.water gauge
" decomposition of methane	=	32.80%
Calculated weight of carbon deposited in t mins (G)	=	0.0322 lb
Average rate of carbon deposition (G/t)	=	1.61×10^{-3} lb/min

CARBON REMOVAL

RUN 17D

TIME	Y	CO_2	CO	K	C_1	C_2	O_1	O_2
5	10.00	18.00	18.32	0.185	1.715	1.72	0.634	0.63
10	9.37	19.65	17.47	0.164	2.180	3.92	-0.564	0.07
15	9.37	19.65	17.47	0.164	2.057	5.79	-0.257	-0.10
20	9.37	18.65	17.47	0.164	1.703	7.49	0.459	0.47
25	9.37	18.54	17.54	0.168	1.655	9.35	0.576	0.05
30	9.37	18.55	17.47	0.164	2.057	11.41	-0.257	0.52
35	9.37	18.73	17.30	0.160	2.145	13.55	-0.477	0.11
40	9.37	18.97	17.13	0.155	1.999	15.48	-0.083	0.03
45	9.36	18.90	16.96	0.152	1.463	16.94	0.835	0.86
50	9.36	18.90	16.96	0.152	2.069	19.01	-0.405	0.45
55	9.06	19.20	16.62	0.144	1.086	20.10	1.515	1.07
60	9.11	19.00	16.70	0.148	2.307	22.60	-1.344	0.63
65	9.16	19.00	16.70	0.148	2.155	24.76	-0.636	-0.00
70	9.01	19.20	16.62	0.144	0.835	25.59	2.030	2.03

TABLE 4.20 RUN 17E

CARBON DEPOSITION

RUN 17E

	Y	CO_2	CO	K	O_1	C_2	O_1	O_2
[illegible]	10.00	10.00	10.32	0.135	1.607	1.61	0.272	0.27
[illegible]	[illegible]	10.00	16.62	0.144	2.083	3.59	−0.302	0.30
[illegible]	[illegible]	10.73	15.76	0.136	2.058	5.73	−0.590	−0.33
[illegible]	[illegible]	10.00	15.25	0.116	1.629	7.39	0.034	−0.33
[illegible]	[illegible]	10.86	15.59	0.122	1.136	8.55	1.130	0.33
[illegible]	[illegible]	10.36	15.59	0.122	2.154	10.70	−0.213	0.21
[illegible]	[illegible]	10.07	15.42	0.119	1.891	12.59	−0.410	−0.40
[illegible]	[illegible]	10.00	15.25	0.116	1.878	14.47	−0.425	−0.32
[illegible]	[illegible]	10.00	15.23	0.116	1.330	15.85	0.278	−0.21
[illegible]	[illegible]	10.00	15.07	0.113	1.758	17.18	−0.253	−0.17

CARBON REMOVAL

Total gasification time (t_1)	=	55 mins
Average pressure of inlet gas (p_2)	=	54.5 ins.water gauge
Total outlet gas flow (V_5)	=	17.22 ft^3
Weight of carbon removed	=	0.0423 lb
Rate of carbon removal	=	0.769 x 10^{-3} lb/min
Weight of oxygen absorbed	=	0 lb
Rate of oxygen absorption	=	0 lb/min

TABLE 4.21 RUN 17F

CARBON DEPOSITION

Total outlet gas flow (V_3)	= 11.25 ft^3
Room temperature (T)	= 21°C
Total reaction time (t)	= 30 mins
Average pressure of inlet gas (p_1)	= 59.8 ins.water gauge
Average decomposition of methane	= 17.4%
Calculated weight of carbon deposited in t mins.(G)	= 0.0237 lb
Average rate of carbon deposition ($G/_t$)	= 0.790 x 10^{-3} lb/min

CARBON REMOVAL

Total gasification time (t) = 55 mins

RUN 17F

[illegible]								

TABLE 4.22 RUN 17G

CARBON DEPOSITION

RUN 17G

TIME	%	CO_2	CO	%	O_2	C_3	O_2	O_2

CARBON REMOVAL

Total gasification time (t_1)	=	45 mins
Average pressure of inlet gas (p_2)	=	55.3 ins.water gauge
Total outlet flow of gas (V_5)	=	14.05 ft^3
Weight of carbon removed	=	0.0358 lb
Rate of carbon removal	=	0.795 lb/min
Weight of oxygen absorbed	=	0.0030 lb
Rate of oxygen absorption	=	0.066 lb/min

RUN 17H

TIME	Y	CO_2	CO	%	O_2	O_2	O_2	O_2

TABLE 4.24

Run No.	CARBON DEPOSITION							CARBON GASIFICATION							
	V_3 (ft^3)	T (°C)	t (mins.)	P_1 ins. water	CH_4 % decomp.	G (lb)	G/t lb/min x 10^{-3}	t_1 mins.	V_5 ft^3	P_2 ins. water	$12\Delta C$ (lb)	$12\Delta C/t_1$	$16\Delta O$ (lb)	$16\Delta O/t_1$	Average K
18	26.25	22	70	37.4	28.0	0.0916	1.308	100	36.60	33.2	0.03489	0.3489	0.04596	0.4596	0.0337
20A	17.5	24	50	13.7	24.9	0.0538	1.076	60	22.60	19.20	0.1299	2.1650	0.0234	0.3900	4.0730
B	43.35	24	120	17.4	29.9	0.1605	1.337	60	22.65	23.42	0.1301	2.168	0.0284	0.4730	4.4860
C	44.60	24	120	17.5	36.3	0.1986	1.655	60	23.10	25.64	0.1382	2.303	0.0254	0.4230	5.9860
D	43.5	24	120	22.3	28.1	0.1516	1.263	60	23.20	34.20	0.1361	2.268	0.0329	0.5480	5.9965
22A	44.3	22	120	26.03	30.3	0.2505	2.087	60	20.73	32.40	0.0603	1.005	0.0038	0.0630	0.1280
B	29.75	23	80	30.2	30.1	0.1110	1.3870	60	20.95	38.94	0.0599	0.998	0.0049	0.0810	0.1036
C	23.6	23	60	22.74	24.9	0.1245	2.075	60	19.20	32.20	0.0386	0.643	0.0170	0.2830	0.2030
D	-	-	-	-	-	-	-	60	19.25	34.86	0.0306	0.510	0.0046	0.0760	0.2990
E	11.85	22	30	23.4	25.3	0.0635	2.116	60	22.35	35.58	0.0311	0.518	0.0737	1.2280	0.052
23A	58.38	23	180	17.5	4.76	0.0449	0.249	60	18.50	28.8	0.0526	0.876	0.0284	0.4730	0.2580
B	99.57	23	300	20.9	6.37	0.1210	0.403	60	18.52	33.4	0.0501	0.835	0.0315	0.5250	0.2970
C	39.35	24	100	23.6	25.0	0.2097	2.097	60	18.70	46.9	0.0842	1.403	0.0364	0.6060	1.486
D	23.55	22	60	25.1	24.2	0.1227	2.045	45	16.10	46.24	0.0059	0.1310	0.0398	0.8840	0.0260
E	24.25	22	60	33.9	47.1	0.1375	2.291	40	15.60	42.68	0.0886	2.2150	0.0231	0.5770	4.298
F	21.25	23	60	24.6	12.0	0.0524	0.873	50	15.35	37.49	0.0375	0.750	0.0292	0.5840	0.2534

Note:- $12\Delta C$ = total carbon removed in t_1 mins, lb .

$16\Delta O$ = total oxygen absorbed in t_1 mins, lb .

CARBON DEPOSITION

Composition of inlet gas :-

Methane (V_1)	=	0.16 ft^3/min
Nitrogen (V_2)	=	0.14 ft^3/min
Average inlet gas pressure (p_1)	=	24.8 ins. water gauge
Room temperature (T)	=	21°C
Reaction temperature	=	1325°F
Total reaction time (t)	=	178 mins
Total outlet gas flow (V_3)	=	65.7 ft^3
Average decomposition of methane	=	30.9 %
Calculated weight of carbon deposited in t mins. (G)	=	0.253 lb
Average rate of carbon deposition ($G/_t$)	=	1.42×10^{-3} lb/min

CARBON REMOVAL

In this run, with a reaction temperature of 1100°F, the carbon removal was achieved by admitting air to the bed in place of carbon dioxide. The exit gas was analysed by conventional absorption gas analysis techniques, and it may be seen from the Table that the oxygen content of the exit gas was almost negligible indicating almost complete utilization.

The carbon removal calculation and oxygen absorption by the bed calculation were done by hand for this run. The carbon removal could be calculated easily from the exit gas analysis and flow, and the oxygen absorption from a combined nitrogen and oxygen balance on the exit gas analysis.

TABLE 4.25

Time (min)	Feed gas	Inlet flow rate ft^3/min	Total outlet flow ft^3	Average pressure (ins. water)	Off-gas analysis% N_2	CO_2	CO	O_2	Calculated results carbon removed lb x 10^{-3}	oxygen absorbed lb x 10^{-3}	K
0	air	0.255	-	-	-	-	-	-	-	-	
5	"	"	1.3	36.8	89.43	1.67	8.28	0.62	4.39	7.66	0.410
15	"	"	4.0	37.0	78.81	6.84	14.35	0.0	19.45	6.31	0.315
30	"	"	8.3	36.6	80.24	7.80	11.25	0.71	27.65	11.54	0.162
45	"	"	12.5	35.4	80.55	7.40	11.92	0.31	27.41	11.20	0.192

5. GENERAL DISCUSSION

The most important points for consideration in the light of the data given in parts 2, 3 and 4 of this work are the following :-

(a) the value of the Boudouard equilibrium ratio obtained for carbon gasified in fixed and fluidized beds.

(b) the rates of carbon gasification, and

(c) the rate of oxygen uptake by the bed of iron powder.

5.1. Boudouard equilibrium ratio value.

It is apparent from the earlier parts of this work that even with the short residence time possible with a small laboratory fluidized bed, a good approach to equilibrium between carbon dioxide and small coke particles is possible. As had been predicted earlier, the values of equilibrium ratio obtained between deposited carbon and carbon dioxide in all cases exceeded the β-graphite, Boudouard equilibrium constants.

It may be seen from the data for Run 16 that when steady state conditions had been achieved during gasification of the carbon on the fluidized bed by carbon dioxide, a virtually constant value of outlet gas composition and therefore a constant value of equilibrium ratio was obtained.

The value of K tends to depart from constancy at the beginning of a gasification cycle due to the inevitable short lapse of time between the analysis by katharometers

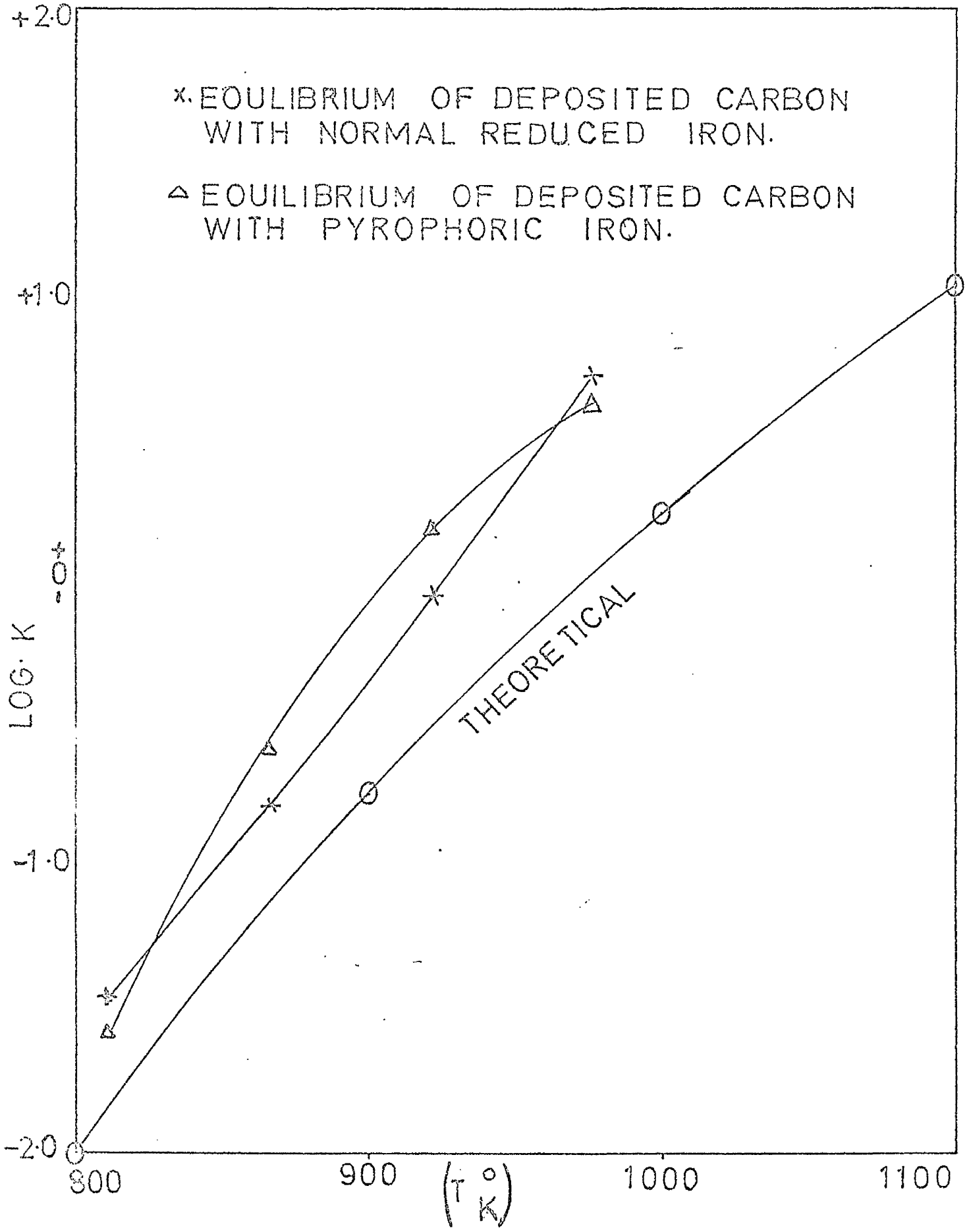
of inlet and outlet gas. Changes in the value of K during the gasification period were largely due to slight fluctuations in the temperature of the bed, and near the end of the gasification, if it was carried on long enough to remove excessive amounts of carbon from the bed. This constancy makes it possible to tabulate average values of K for steady state condition and these values are to be found in the data for each cycle of run. The average value for each overall run was then obtained and these are tabulated in Table 4.26.

It can be seen that the equilibrium ratios for Run 16 to 23 (in the temperature range 1000° - 1300°F) for carbon deposited on reduced iron (either stable or pyrophoric) are much higher than those which have been reported for β-graphite in the same temperature range. The difference between these two series of values can be seen much more precisely in Figure 4.12 and indicates that the deposited carbon has an excess value of free energy.

The excess free energy of the deposited carbon was calculated in the conventional manner from the values of K obtained here, and the results obtained are tabulated in Table 4.26. As may be seen, the values of excess free energy range from 1.07 Kcal/gm.mole to 3.08 Kcal/gm.mole according to the reaction temperature. These values compare very well with those reported by Squires[43] for methane synthesis reactions. This excess free energy

TABLE 4.26

Run No.	Temperature °F	Temperature °K	EQUILIBRIUM RATIOS K	EQUILIBRIUM RATIOS log K	ΔF, Cal/gm.mole Theoretical	ΔF, Cal/gm.mole Theoretical	ΔF, Cal/gm.mole Experimental	Excess free energy Cal/gm.mole
16	1200	922	0.8790	-0.0601	-0.6000	2200	254	1946
17	1100	866	0.1583	-0.80051	-1.1900	4550	3160	1390
18	1000	811	0.0337	-1.47237	-1.8200	6950	5470	1486
20	1300	977	5.1363	+0.71062	-0.0600	-100	-1381	3081
22A	1100	866	0.1288	-0.89007	-1.1900	4550	3530	1020
B	"	"	0.1036	-0.98462	"	"	3900	650
C	"	"	0.2030	-0.69250	"	"	2745	1805
D	"	"	0.2990	-0.52433	"	"	2075	2475
E	"	"	0.520	-1.28400	"	"	5080	-
23A	1100	866	0.258	-0.58838	-1.1900	4550	2335	2215
B	"	"	0.297	-0.52724	"	"	2095	2455
C	1200	922	1.486	+0.17203	-0.600	2200	728	1472
D	1000	811	0.026	-1.58503	-1.8200	6950	5880	1070
E	1300	977	4.298	+0.63358	-0.0600	-100	-2835	2735
F	1100	866	0.2534	-0.59620	-1.1900	4550	2369	2181

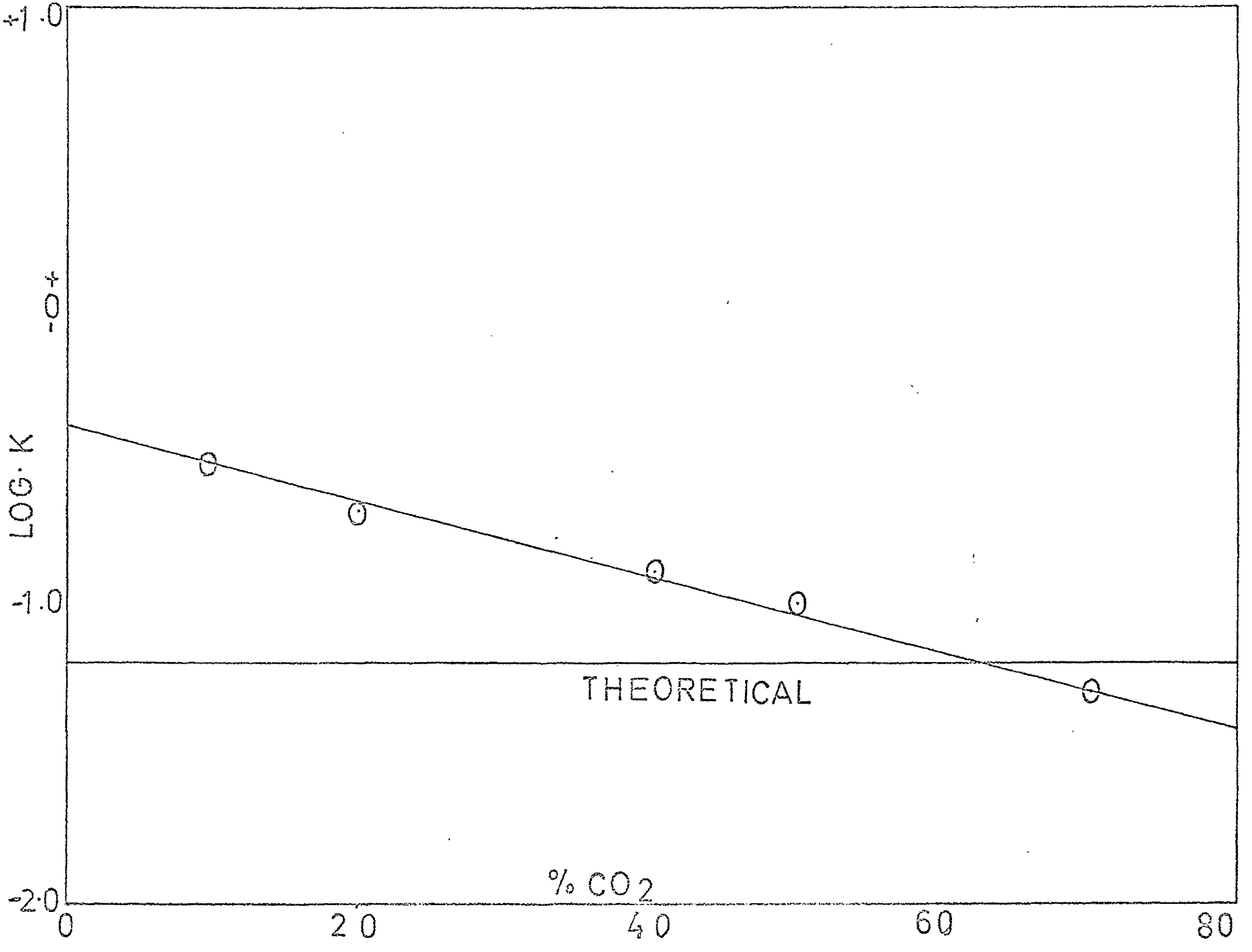

+2·0
+1·0
-0·
-1·0
-2·0
LOG K
800
900
1000
1100
(T °K)
EQUILIBRIUM OF DEPOSITED CARBON WITH NORMAL REDUCED IRON.
EQUILIBRIUM OF DEPOSITED CARBON WITH PYROPHORIC IRON.
THEORETICAL

FIG·4·12

provides a convenient measure of the reactivity of this deposited carbon when compared with some standard substance such as β-graphite. The practical significance of this carbon reactivity is that it should be possible on an industrial scale to generate carbon monoxide in high yield at a relatively low temperature.

In a cyclical process using a solid powder as catalyst one is always concerned to find the "life" of this catalyst. As explained the iron powder used in this work was simply derived from an iron ore. If this process was carried out industrially, a specially prepared iron catalyst would probably be necessary, since it has been found that after about sixteen cycles of operation, breakdown of the iron particles had taken place to such an extent that excessive amounts of the bed were being blown out of the reactor. This breakdown of the iron particles does not appear to affect greatly the value of K obtained until it has proceeded to such an extent that the reduction of overall particle size in the bed increases the violence of fluidization. This has the effect of increasing K further (e.g. Run 16J and K).

In Run 22, the concentration of carbon dioxide was varied between 10% and 70% of the inlet gas. The values of K for the outlet gas corresponding to the inlet values are plotted in Figure 4.13. It may be seen that the values of K except in the case of 70% carbon dioxide inlet



FIG· 4·13

gas, are all greater than the value for β-graphite. As the initial concentration of carbon dioxide is increased the value of log K falls linearly indicating that at the temperature employed the residence time was insufficient to allow complete reaction of the carbon dioxide. This suggests that with a deeper bed and low concentration of inlet carbon dioxide much higher values of K would have been obtained indicating that the deposited carbon is even more reactive than is suggested by the values of "free energy" that have been quoted above.

5.2. Rate of carbon gasification.

The rate of gasification of the carbon deposited on the bed of iron powder will be dependent possibly on the following :-

(a) reaction temperature,

(b) concentration of carbon dioxide in the inlet gas,

(c) extent of coverage of iron by carbon, and

(d) state of oxidation of iron catalyst.

If one considered only the values of K obtained during a gasification run, it would be somewhat difficult to know the exact instant when all the carbon on the bed was gasified. Since the reaction

$$C + CO_2 = 2\,CO$$

$$Fe + CO_2 = FeO + CO$$

are taking place side by side, the removal of all the carbon would cause the value of K to move from the value

for the Boudouard reaction to that for the reaction of iron and its oxides with carbon dioxide. The measurement of carbon removal by means of a carbon balance and the uptake of oxygen by the bed by means of an oxygen balance enable one to study these two reactions separately.

The data provided by the computor enabled us to plot the weight of carbon removed from the bed for any run against time. This has been done in Figure 4.14 for a number of runs selected at random. In cases where the removal was stopped while some carbon still remained on the bed, the rate of removal may be seen to be constant and thus independent of the amount of carbon on the bed. Since as will be seen later, the iron was oxidising at the same time, it would appear that the rate of removal of carbon is independent of the state of oxidation of the iron for the small amounts of oxygen absorbed by the bed.

In Run 17H the carbon dioxide was passed through the bed for a considerable time in an attempt to remove all the carbon from the bed. It may be seen that after about 210 minutes of run the rate of removal departed from linearity and the computor data gave a number of negative results. The latter are possibly due to inlet flowrate fluctuations which are not immediately followed by the katharometers. When a series of negative values are obtained in this way, it must be taken as an indication that the carbon has all been removed.

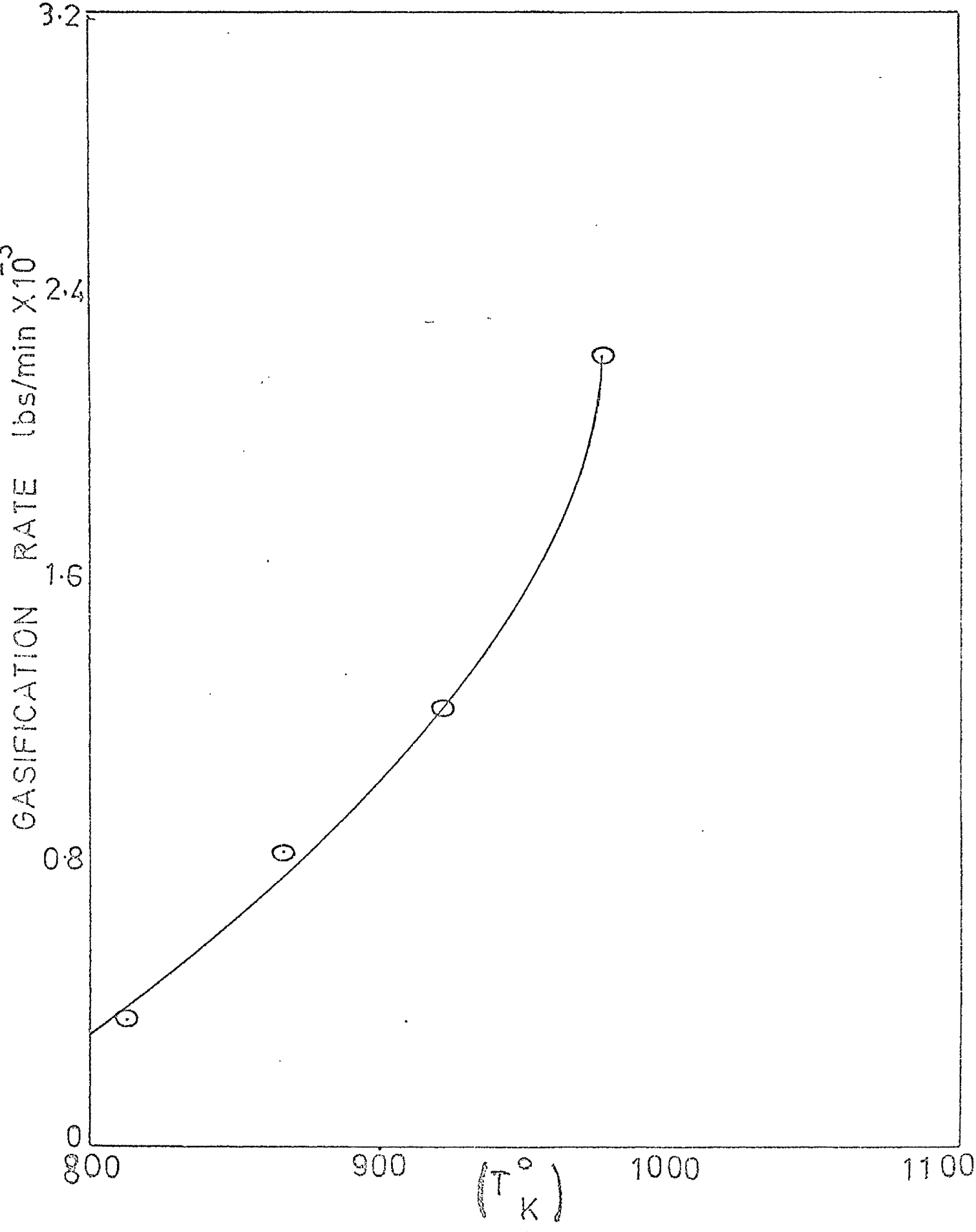
0
CARBON REMOVED, gms
20B
16C
22A
23B
18
17H
120
240
360
480
TIME

FIG. 4.14

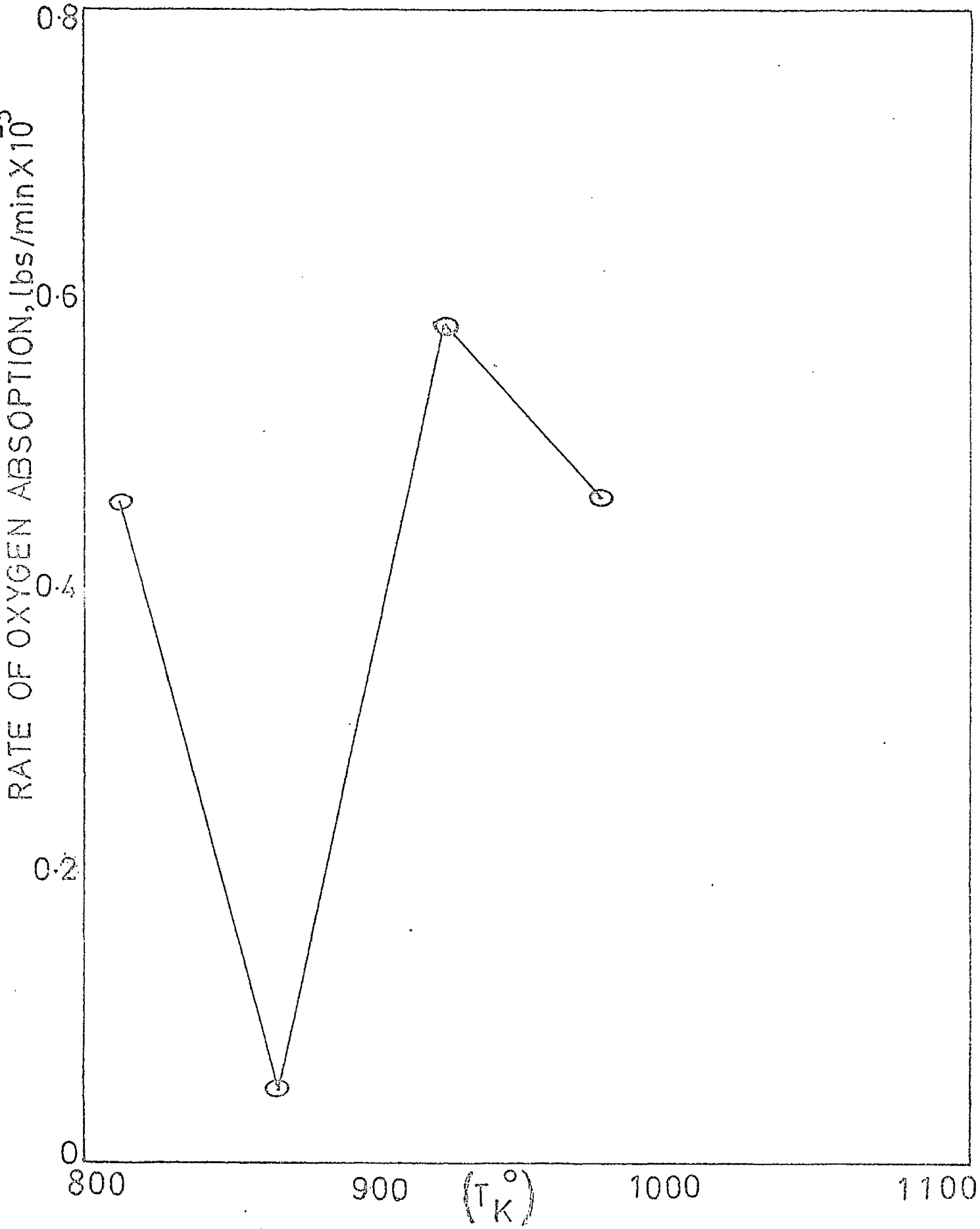
The average rates of carbon removal and oxygen uptake for the various run cycles quoted earlier have been tabulated for convenience in Table 4.24. Average values for each of Runs 16, 17, 18 and 20 are plotted against reaction temperature in Figure 4.15 and Figure 4.16.

It may be seen that the rate of gasification is approximately proportional to the reaction temperature, up to about 1200°F and thereafter increases rapidly. In order to compare this reactor with a conventional gas producer, operated at a considerably higher temperature, the rate of gasification per square foot of reactor area was calculated and is included in Table 4.27. By normal producer standards these rates are low, but are in fact high when the reaction temperature is considered.

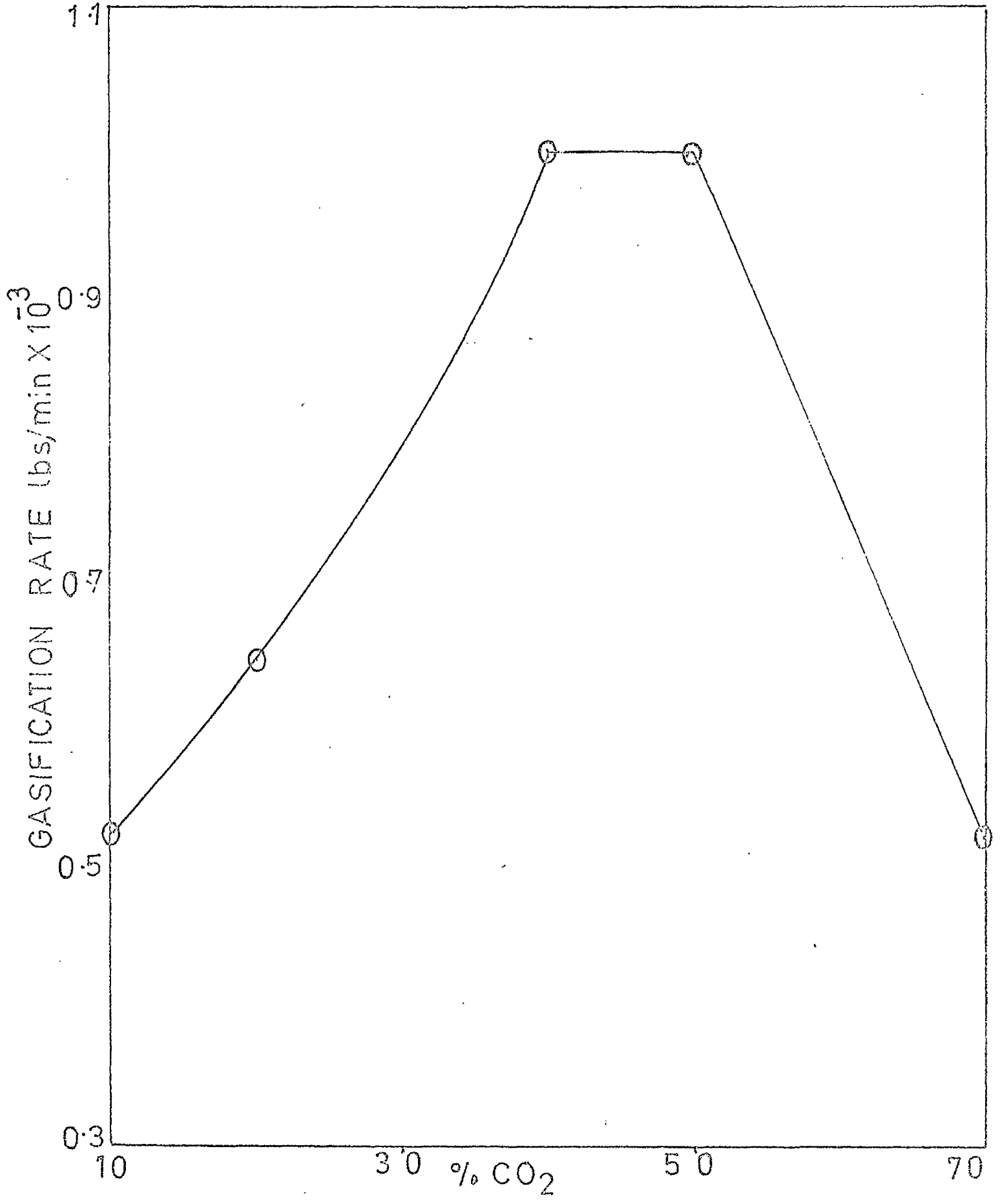
In Run 22 in which the inlet concentration of carbon dioxide was varied, the rate of gasification was also found to change to some extent. These results are plotted in Figure 4.17 and it is seen that the rate appears to pass through a maximum at about 40% carbon dioxide in the inlet gas. This is probably due to the retarding effect of carbon monoxide on the reaction between carbon and carbon dioxide which has been reported by Hinshelwood[56]. If air is used to gasify the carbon in place of carbon dioxide, the maximum initial concentration of carbon dioxide at the base of the bed cannot rise above 21% and thus the retarding


3·2
2·4
1·6
0·8
0
GASIFICATION RATE lbs/min X10⁻³
800
900
1000
1100
(T° K)

FIG·4·15


0·8
0·6
0·4
0·2
0
RATE OF OXYGEN ABSOPTION, lbs/min X 10⁻³
800
900
(T K°)
1000
1100

FIG·4·16



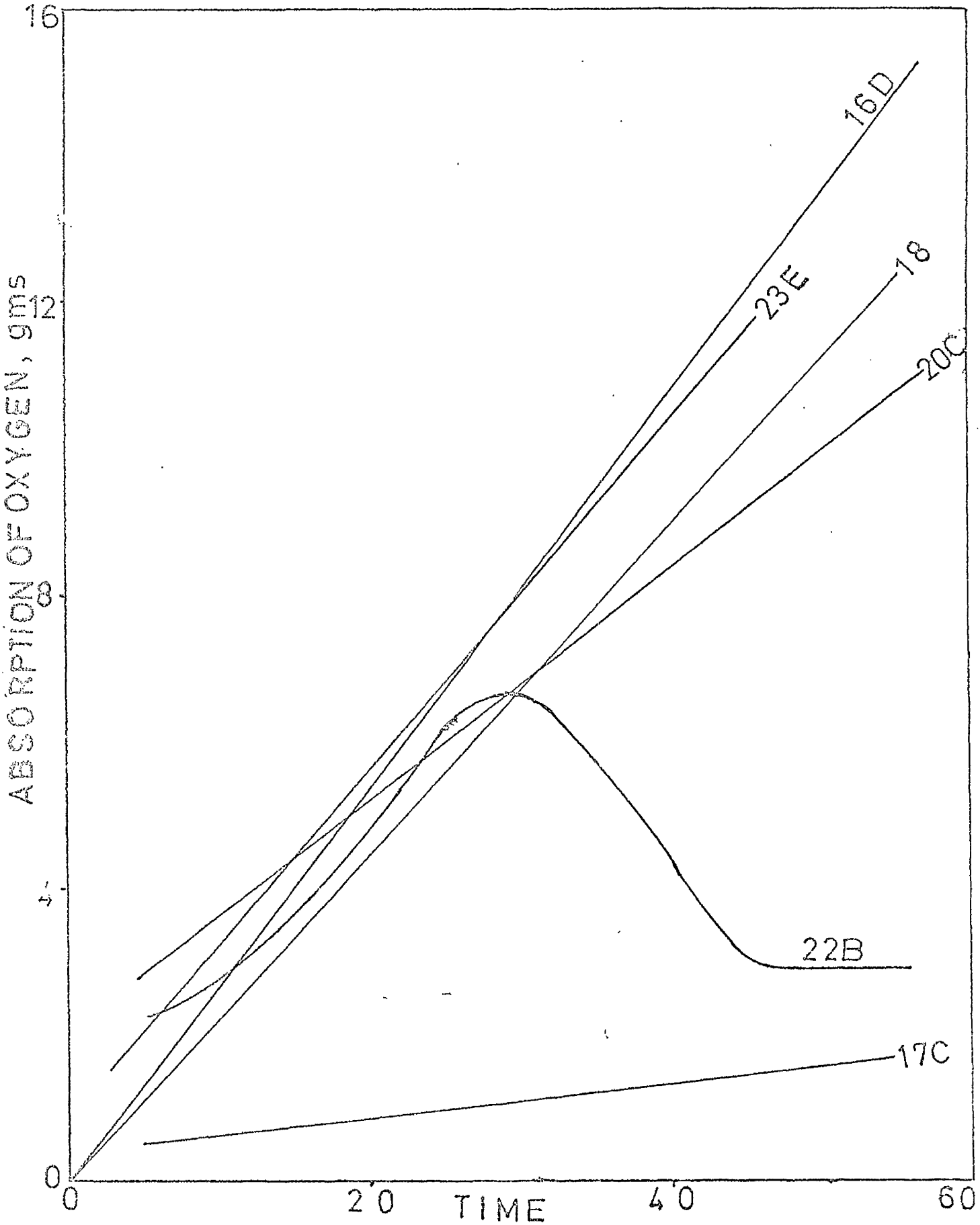
FIG·4·17

effect is of little importance. On the other hand, if the reactor is fed with oxygen-enriched air or pure oxygen the possible initial carbon dioxide content at the base of the reactor will be much higher and thus the use of oxygen will be limited by the carbon monoxide retarding effect.

5.3. Rate of oxygen absorption by the bed.

In Figure 4.18 are plotted the weights of oxygen absorbed by the bed against run time for sets of data selected at random. Except in one case the plots show a linearity with time and thus it would appear that the rate of oxygen uptake is unaffected by the amount of carbon on the bed. It is interesting to speculate on whether it is possible to cover the iron with carbon so that the carbon dioxide cannot reach it. There has been no evidence of that here and some oxidation has always been found to take place.

The oxygen absorption in Runs 17 and 22 carried out at 1100°F is in general anomalous in that it is considerably lower than that for other temperatures and in the case of 22B is negative for a period. This is illustrated in Figure 4.18. No adequate explanation for this can be given at the moment. The rates of oxygen absorption tabulated in Table 4.27 are all considerably smaller than the rates of carbon removal even when the difference between the atomic weights of carbon and oxygen are taken into consideration.


16
12
8
4
0
ABSORPTION OF OXYGEN, gms
16D
23E
18
20C
22B
17C
0
20
TIME
40
60

FIG·4·18

TABLE 4.27

Run No.	Temp. °F	GASIFICATION RATE			OXYGEN ABSORPTION RATE	
		lb/min x 10^{-3}	lb.atom/min. x 10^{-5}	lb/ft^2-hr.	lb/min. x 10^{-3}	lb.atom/min. x 10^{-5}
16	1200	1.236	10.30	1.795	0.5800	3.62
17	1100	0.820	6.83	1.191	0.052	0.320
18	1000	0.3489	2.90	0.506	0.4596	2.87
20	1300	2.226	18.55	3.233	0.458	2.86

5.4. Composition of bed at end of run.

At the end of Runs 18 and 23 the bed was removed, thoroughly mixed and a representative sample taken for analysis by the methods given earlier. The bed compositions are tabulated below :-

TABLE 4.28

Composition of fluidized bed at end of run (percentages by weight).

	Run 18	Run 23
Iron	81.90	67.65
Carbon	3.97	15.55
Gangue	5.88	4.85
Oxygen	8.25	11.95
	100.00	100.00

As has been shown, it was possible to estimate with a fair degree of accuracy the carbon content of the bed at any time. Owing, however, to the reduction of iron to an unknown extent by hydrogen liberated from methane during the carbon deposition, i.e.

$$CH_4 = C + H_2$$

$$H_2 + FeO = H_2O + Fe$$

$$H_2O + C = H_2 + CO$$

$$CO + H_2O = CO_2 + H_2$$

we were unable to calculate an oxygen balance for the process. The extent of oxidation of the iron residues in Table 4.28 correspond to the following empirical formulae

Run 18, $FeO_{0.352}$

Run 23, $FeO_{0.62}$

This indicates quite a small degree of oxidation of the iron by carbon dioxide.

5.5. Efficiency of carbon dioxide utilization.

In this gasification process it may be considered that carbon dioxide reacting with carbon is usefully employed and the carbon dioxide oxidising iron is wastefully employed. If one calculates the proportion of the total carbon dioxide used for each reaction one may derive an efficiency of utilization for the process, as follows :-

$$CO_2 + C = 2\,CO$$

Each atom of carbon gasified ≡ 1 mole CO_2

$$CO_2 + Fe = FeO + CO$$

Each atom of oxygen absorbed ≡ 1 mole CO_2

∴ Rate of carbon dioxide utilization (moles/min) = Rate of gasification (atoms C/min) + Rate of oxygen absorption (atoms O/min)

∴ Efficiency of carbon dioxide utilization

$$= \frac{\text{(Rate of gasification)}}{\text{(Rate of carbon dioxide utilization)}} \times 100$$

From the data given in Table 4.27 the required values are easily obtained and are given below for Runs 16 - 20.

TABLE 4.29

Run No.	Reaction temperature °F	Efficiency of carbon dioxide utilisation. (%)
16	1200	74.0
17	1100	95.5
18	1000	50.2
20	1300	86.6

These values are plotted in Figure 4.19 against reaction temperature and it may be seen that except in the case of Run 17 the efficiency increases regularly with reaction temperature. This indicates that this gasification process would operate more efficiently at a high temperature, perhaps 1400°F or a little higher.

In conclusion the results illustrated in Figure 4.12 are of considerable interest since they indicate that carbon deposited on pyrophoric iron is more reactive than that deposited on iron reduced at a higher temperature. This suggests that the reaction scheme is linked in some way to the catalytic activity of the reduced iron.

FIG. 4.19

5.6. Suggestions for further work.

In the light of the results obtained the following suggestions are made for further study.

(a) Owing to the variability of the composition of the iron ore and to the fact that the iron particles produced from it have been found to disintegrate after some hours in the gasification process, it is suggested that further work be carried out using a synthetic catalyst based on pure ferric oxide and a binding agent.

(b) The effect of the depth of the fluidized bed of deposited carbon on the equilibrium ratio should be studied, in connection with inlet gases containing low partial pressure of carbon dioxide to determine the maximum value of K obtainable at a given temperature.

(c) The classical studies of Hinshelwood et al on coconut charcoal could well be repeated using carbon deposited from the thermal cracking of methane.

(d) Other industrial gases, i.e. Propane and Butane should be studied as sources of deposited carbon and the results obtained compared with those recorded here.

(e) The influence of the temperature of reduction of the iron on the reactivity of the deposited carbon should be more fully investigated.

(f) By means of careful and, if possible, continuous analysis of the exit gases during the carbon deposition, the extent of which the iron is re-reduced by the methane may be determined and an overall oxygen balance can be obtained.

(g) The gasification unit should be modified to allow samples of the bed to be withdrawn for analysis at any time during a run.

(h) The arrangement of the exit cyclone should be changed so that solids blown from the bed could return to it continuously during a run. This would enable higher fluidizing velocities to be used and the effect of fluidizing velocity on the rate of gasification could then be studied.

(i) An experimental twin-gasifier should be built to enable carbon deposition and carbon gasification to be carried out simultaneously, and a change-over valve system be provided to determine whether it is possible to produce virtually continuous streams of hydrogen-rich (and carbon monoxide-free) and carbon monoxide-rich (and hydrogen-free) gases for later blending in required proportions for synthesis gas.

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